

2002 Microgravity Materials Science Conference

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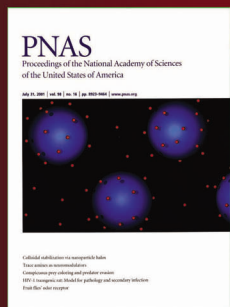
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Materials Science in the News



Dr. Jennifer Lewis, University of Illinois at Urbana-Champaign

Negligibly charged colloidal microspheres (blue) aggregate in aqueous solution but undergo a stabilizing transition upon addition of highly charged nanoparticles (red). This type of self-organization, or haloing, provides a new method for tailoring the behavior of complex fluids.



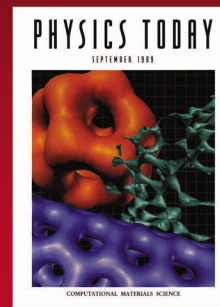
Professor Gregory Rohrer, Carnegie Mellon University

Interference contrast micrograph of an oxidized titanium polycrystal. A thin film of rutile (TiO_2) was grown on the surface by heating the sample in air for 1 hour at a temperature of 700 °C. The difference in color between individual grains is a result of the variation in film thickness across the sample (Width of micrograph: ~220 nm).



Professor Mark Hollingsworth, Kansas State University

Modern crystal engineering has emerged as a rich discipline whose success requires an iterative process of synthesis, crystallography, crystal structure analysis, and computational methods. By focusing on the molecular recognition events during nucleation and growth, chemists have uncovered new ways of controlling the internal structure and symmetry of crystals and of producing materials with useful chemical and physical properties.



Professor Jerry Bernholc, North Carolina State University

Calculated electron distribution in fullerenes, a new class of materials with remarkable properties. Clockwise from top, C_{60} , C_{36} , and a carbon nanotube. The electron distribution, which completely determines the ground-state properties, was obtained by large-scale, supercomputer calculations.



Professor Michael Tsapatsis, University of Massachusetts

Crystalline molecular sieves like zeolites, play a major role in catalysis, adsorption, and ion exchange. In the form of thin films (left) they can be used as membranes, membrane reactors, sensors, microreactors, corrosion protective coatings, in thermoelectric devices, as low dielectric constant materials and in many other novel applications. Single crystals of these materials, appropriately incorporated in devices (right), can find use in sensing, optical, and electronic applications. Continuing progress in understanding and controlling their growth, structure and properties is expected to sustain their major role in the chemical process industries and may enable their use in novel applications.



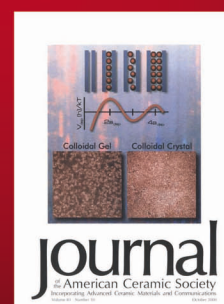
Professor Gregory Rohrer, Carnegie Mellon University

An interference contrast micrograph of a SiC growth surface. The 6H SiC crystal was grown by the seeded sublimation method at 2300 °C. The micrograph illustrates the point at which trains of growth steps from nearby sources (super screw dislocations) impinge. The steps originating from the lower right are almost ideal concentric circles. The steps progressing from the upper left exhibit instabilities, possibly caused by pinning points or competitive sources.



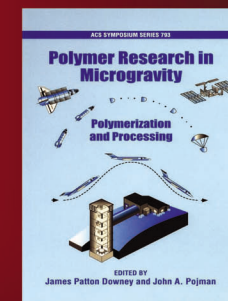
Dr. Richard Weber, Containerless Research, Inc.

Liquid aluminum oxide (3 mm) that has been levitated by a gas jet, stabilized by acoustic forces, and heated at 2700 kelvin in a carbon dioxide laser beam. Levitation of high-temperature liquids with optical access for measurement instruments will contribute to 21st century Gordon Research Conferences on High-Temperature Materials, Processes, and Diagnostics.



Dr. Jennifer Lewis, University of Illinois at Urbana-Champaign

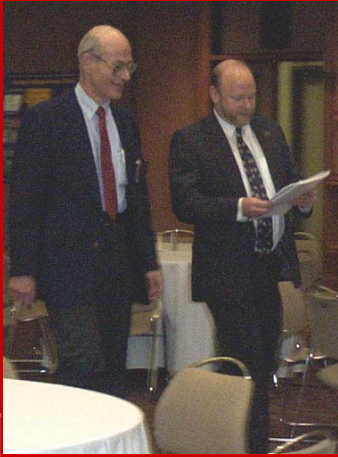
Colloidal processing of ceramics is reviewed with an emphasis on interparticle forces, suspension rheology, consolidation techniques, and drying behavior. Particular attention is given to the scientific concepts that underpin the fabrication of particulate-derived ceramic components. The complex interplay between suspension stability and its structural evolution during colloidal processing is highlighted.



Dr. James Patton Downey, NASA MSFC and Dr. John Pojman, University of Southern Mississippi

This publication reviews the history of polymeric microgravity research, discusses polymeric systems most affected by gravity, and speculates on the future of microgravity polymeric research.

Conference Photos



Conference Photos



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Marshall Space Flight Center Space Science News

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2002 Microgravity Materials Science Conference

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Proceedings of a conference sponsored by the
Physical Sciences Division, NASA Headquarters,
organized by the Materials Science Working Group
and held at Huntsville, Alabama, June 25-26, 2002

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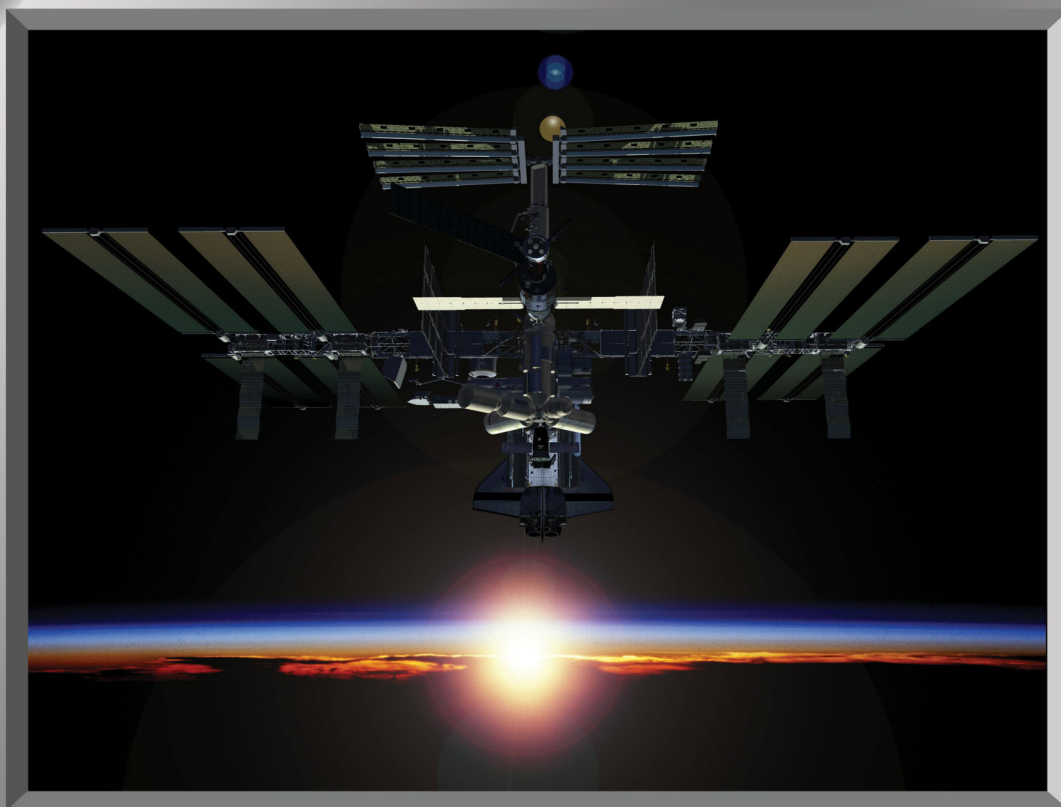
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2002 Materials Science Conference



A new dawn . . . a new direction

June 25–26, Von Braun Center, Huntsville, Alabama

Hosted by
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Sponsored by
The Physical Sciences Division, NASA Headquarters, Washington, DC

Organized by
The Materials Science Discipline Working Group

Foreword

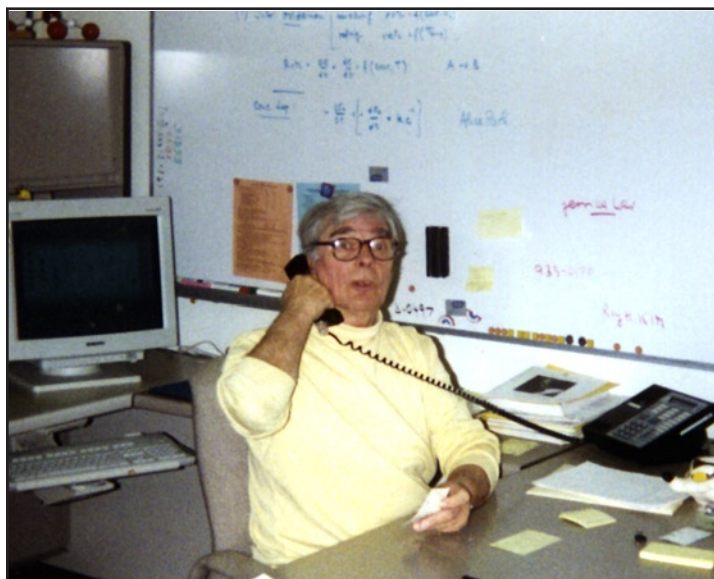
The 2002 Microgravity Materials Science Conference was held June 25-26 at the Von Braun Center, Huntsville, Alabama. The fifth of its kind, it was organized by the Microgravity Materials Science Discipline Working Group, sponsored by the Physical Sciences Research Division, NASA HQ and hosted by NASA Marshall Space Flight Center (MSFC) and member institutions under the COoperative Research in Biology and Materials Science (CORBAMS) agreement. The conference provided a forum to review the current research and activities in materials science, to discuss the envisioned long-term goals, to highlight new crosscutting research areas of particular interest to the Physical Sciences Research Division, and to inform the materials science community of research opportunities in reduced gravity. The conference featured a plenary address by Dr. Ron Litchford (MSFC) on “Future Space Transportation” on the opening day followed by oral presentations from selected Principal Investigators in the Materials program. The speakers were selected by the discipline working group based on a review of the submitted abstracts, novelty of results, and overall maturity of the research program. Selected oral presentations were also scheduled for the second day of the conference. No concurrent talks were scheduled, thus allowing all participants to attend all presentations. A dedicated poster session was held in the afternoons on both days.

An abstract book was published and distributed at the conference. Conference attendance was about two hundred and forty people with representation from industry, academia and other NASA centers. The conference featured several exhibits highlighting the resources and capabilities of MSFC’s Microgravity program and other exhibits from external vendors. These included a full-scale mock-up of the US Destiny module from the International Space Station containing the materials science research rack and the microgravity science glovebox. Also on display were the ground units for the first two materials science glovebox investigations slated for later in 2002. The conference reception and banquet were held at the Huntsville Hilton, and included an address by Dr. Michael Houts on “Fission Systems for Enabling Exciting Space Missions.” This CD ROM of the conference proceedings is comprised of research reports submitted by the Principal Investigators in the Microgravity Materials Science program.



Conference attendees and the Destiny Space Station Module in the main conference room at the 2002 Microgravity Materials Science Conference, Huntsville, Alabama, June 25-26, 2002.

In Memoriam: August Witt, 1931-2002



"If you're really interested in exploring the unknown, how can you not be attracted to NASA?" - August Witt

August F. Witt, a stalwart supporter of NASA's Materials Science program, died October 7, 2002 of gastric cancer at his home in Winchester, MA. Professor Witt was born in Innsbruck, Austria, in 1931. From 1953-54 he did graduate research in nuclear chemistry with Madame Joliot-Curie, a 1935 Nobel laureate, in Paris. In 1958 he worked on radiation chemistry at the Atomic Energy Research Establishment in Harwell, England. He received his Ph.D. in 1959 in physical chemistry from the University of Innsbruck.

Professor Witt joined MIT in 1960 as a research associate and worked on surface chemistry problems related to mineral flotation. In 1962 he was appointed to the faculty as an assistant professor and his primary research focus

became the processing and characterization of electronic materials. He was promoted to professor in materials science in 1972.

With colleague, Professor Harry Gatos, Professor Witt was responsible for one of the most important experiments for advancing materials processing in space. The growth of Te-doped indium antimonide on the Skylab, and later Ga-doped germanium on the Apollo-Soyuz mission verified fundamental theories of plane front solidification in doped materials. The dramatic size increase obtained in silicon wafers in the last 30 years can in part be contributed to these findings. For this work he received NASA's Outstanding Scientific Achievement Award in 1974.

In 1976 Austria presented him with the Exner Medal for Outstanding Contributions to Science and Technology. Professor Witt was a member of the American Association of Crystal Growth (past President 1975-1981), the American Ceramic Society, Sigma Xi and Tau Beta Pi. He chaired NASA's Electronic Materials Working Group from 1982-89.

More recently, Professor Witt has been the principal investigator on a NASA flight experiment designed to study the reasons behind the formation of native defects in photorefractive bismuth sillenite crystals. At the time of his death, he was preparing for a science concept review. In these times of reduced budget, he was an active advocate for NASA's materials science program, and wrote many letters to Senators and Congressmen.

Professor Witt was responsible for guiding and encouraging many scientists from MIT and other universities into NASA's programs, and can be regarded as the father figure of microgravity materials science. His students and associates have been major contributors in developing fabrication and characterization techniques of electronic materials. He will be sorely missed.

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INVESTIGATING MORPHOLOGICAL STABILITY OF FACETED INTERFACES WITH AXIAL HEAT PROCESSING (AHP) TECHNIQUE

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Abstract

Successful processing of homogeneous semiconductor single crystals from their melts depends strongly on precise control of thermal and fluid flow conditions near the solid/liquid interface. In this project, we utilize a novel crystal growth technique called Axial Heat Processing (AHP) that uses a baffle, positioned inside the melt near the interface, to supply and/or conduct heat axially to the interface. The baffle, which may or may not have a heater encased in it, can promote more stable and planar growth as well as reduce buoyancy driven convection. The latter is because the baffle reduces the aspect ratio of the melt as it separates the melt into three sections, above the baffle, in the feed gap between the baffle and the crucible wall, and below the baffle between the baffle base and the interface. AHP also enables a close monitoring and/or control of thermal boundaries near the solid/liquid interface during crystal growth by means of thermocouples placed in the baffle. The interface is kept planar when a heating element in the baffle is used. However, a proper choice of melt height is necessary to keep the interface planar when using the baffle without a heater. This study addresses the influence of melt height and growth velocity on the segregation profile of AHP-grown Sb doped Ge single crystals.

Introduction

Homogeneous single crystals of doped semiconductor materials are valuable to the electronic industry. The current Ultra Large-Scale Integration (ULSI) demands that the many wafers, cut from a melt-grown crystal, have consistently uniform electrical properties. This ensures a higher reproducibility and yield of solid-state devices. The solid/liquid (s/l) interface shape and convection in the melt mainly affect the homogeneity (e.g., solute segregation) in melt-grown crystals. A non-planar s/l interface can give rise to accumulation of the solute at depressed levels of the interface due to the gravity. Similarly, buoyancy driven or forced convection could cause fluctuations in the solute distribution at the interface. Since an uneven distribution of dopant results in the undesirable variation of electrical properties, several techniques have been utilized to eliminate segregation during crystal growth. These include the use of controlled thermal boundaries, magnetic fields, low gravity, and continuous feeding procedures¹⁻⁶. These methods focus on two principal factors to control segregation: the s/l interface shape and convection.

To achieve a homogeneous single crystal, it is clear that both convection and the s/l interface shape must be closely controlled. Current techniques to grow single crystals from the melt, such as the Czochralski, Float Zone, and Bridgman techniques, supply heat to the melt from radial sources. This leads to increased convection and non-planar interfaces¹. However, an alternate, novel processing technique called Axial

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Heat Processing (AHP) was developed in Russia to promote stable, planar crystal growth⁷. This technique has been used to grow single crystals with promising success⁸⁻¹². A comparable technique called the Submerged Heater Method (SHM) is currently under investigation by Ostrogorski et. al.¹³⁻¹⁵

AHP technique makes use of a baffle submerged in the melt near the s/l interface. The baffle may have a heater encased in it to supply heat axially to the growth interface. In the case when there is no heater in the baffle, the baffle may be made of a high conductivity material to still conduct the heat axially and distribute it over the growth interface. There are several advantages to having a baffle in the melt. First, the baffle minimizes the radial temperature differences created by the outside (background) heaters, promoting stable, planar growth. Second, the baffle separates the melt into two large regions. This effectively reduces the melt height above the interface, lowering the amount of buoyancy driven convection in that region. Third, by separating the melt into two regions, AHP can utilize the technique of Zone Leveling with starting charge only procedure^{14, 16, 17} to spread the dopant more evenly along the length of the crystal. Fourth, since the AHP method can promote planar growth and makes provisions to closely monitor the temperature of the growth domain, it is a suitable technique for studying interfacial kinetics and morphological stability.

The latter is the subject of current NASA supported international work exploring the fundamentals of faceted single crystal growth. This paper discusses the use of the AHP method to grow single crystals of Ge doped with Sb. AHP growth using a baffle with and without a heater is assessed. Influence of the melt height and growth velocity on the s/l interface shape, radial solute distribution, and morphological stability is analyzed. Some preliminary results have been already published elsewhere¹⁸⁻²⁰.

Experimental

Apparatus

Two different AHP units were used to grow Ge-Sb single crystals, one with a heater in the baffle and one without. Figure 1 shows a schematic of the AHP Unit-1. In this unit, the baffle (1) consists of a graphite shell encasing four C-type thermocouples and a Mo heating element (1-1). Two of the thermocouples record the temperature at the center of the baffle and the other two at the edges of the baffle near the crucible wall. All four are in the same plane, parallel to the base of the baffle. The crucible (2) is also made of graphite, and it has an internal diameter of 46 mm that holds the charge (C1 and C2) and a 20-mm thick disc-shaped seed (3). The charge may be placed in the crucible with two different compositions (C1 and C2), or it may be homogeneous. C₁ and C₂ regions are linked by a feed gap between the baffle and the crucible wall. The width of this channel is small enough (~ 0.5 mm) to prevent any back diffusion from the region below the baffle (C1) to the region above the baffle (C2)²¹. A cap (4) closes the crucible. The crucible is supported by a graphite pedestal (5) and a water-cooled Mo rod (6) that help extract heat from the growing crystal. During growth, the crucible is pulled down through a stationary, graphite guide tube (7). The guide tube is surrounded by a 4-zone background heater (furnace) (8), which provides heat to melt the charge and a portion of the seed. Additional thermocouples are located at strategic positions throughout the crucible, pedestal, and guide tube. A total of 19 thermocouples (T1-T19) monitor and/or control the thermal conditions in the unit. All of these components of the AHP unit are encased in a chamber, in which a vacuum/inert gas environment can be created.

Figure 2 shows a schematic of the AHP Unit-2. This unit also uses a graphite baffle (1) submerged in the melt near the solid/liquid (s/l) interface. However, no heater is placed in the baffle. The charge material is held in a 38.1-mm inner diameter graphite crucible (2), which again may have two different compositions

(C1 and C2) as explained above. A 20-mm high graphite insert (3) with a funnel shape cavity is also placed in the crucible to facilitate single crystal growth from a seed (4) of 5x5x17 mm prismatic shape. A cap (5) closes the crucible to prevent any loss of evaporates. A 3-zone radially heating vertical, tubular furnace (background heater) (6) supplies the required heat to melt the whole charge and a portion of the seed. Heat is extracted axially from the grown crystal through a graphite pedestal (7) and a Monel pedestal rod (8) by natural conduction (no water cooling). Ten calibrated K-type Inconel sheathed thermocouples (T1-T10) are positioned throughout the furnace, pedestal, crucible, and the baffle to control/monitor the thermal profiles. LabTech software controls the background heater zones with PIDs. A quartz retort (9), placed inside the background furnace, encases the aforementioned parts of the AHP unit and serves to create an inert gas atmosphere for the growth.

Procedures

In order to prevent evaporation of low melting point (630°C) Sb during heat up, a master charge of Ge-Sb alloy was prepared, which was then placed on the seed, and pure Ge chunks filled the crucible. The baffle was placed at the top of the solid charge. After positioning the crucible inside the furnace, the background heater was turned on to melt all of the charge and a portion of the seed. Next, the baffle was brought down until a desired initial melt height between the baffle and the seed is established. The baffle then was moved up and down a couple of times to stir the melt in order to create a homogeneous melt. Then, the growth was initiated by lowering the crucible, while the baffle and the background heaters (furnace) stayed stationary. The whole process took place under a slight argon overpressure. Experimental parameters of the crystals grown are given in Table I.

After growth, the samples were cut in half along their longitudinal axes and subsequently analyzed. One half of each sample was polished to a 1-micron finish using conventional metallographic techniques, and four-point probe resistivity measurements were taken to determine the Sb distribution in the samples. The resistivity measurements were done with a ~5 mm interval in radial and longitudinal directions, covering the entire surface of the half-cut sample. Finally, the samples were repolished to a 0.3-micron finish and etched with a 25:3:2 solution (by mass) of water, KOH, and $K_3[Fe(CN)_6]$ at 100°C for approximately 3 minutes to reveal microstructure, especially any possible growth striations.

Numerical Modeling

Crystal growth with the AHP Unit-1 was modeled using finite difference method in a two-dimensional cylindrical (r, z) coordinate system with the origin located at the bottom of the crucible (see Fig. 3). The movement of the incompressible viscous liquid in the melting zone was found by solving the Navier-Stokes equations with the Boussinesq approximation. The equations were written in a vorticity-Stokes stream function formulation. In the melt zone, both heat and solute transport were considered.

The solution of the transient solidification problem included explicit tracking of the solid/liquid interface. At each time step, the new location of the interface was determined. The Stefan condition as well as continuity at the interface was used for temperature, whilst a mass balance was used for the concentration. At the crucible walls, unsteady experimentally measured temperature values were imposed. At the axis of the cylinder (crystal), temperature and concentration fluxes were set to zero, as was the concentration flux at the free surface. At the other boundaries, continuity conditions for temperature and heat flux were imposed. Since a dilute alloy was considered, the melting temperature was taken as constant and equal to melting temperature of Ge.

The equations were non-dimensionalized using the following scaling factors: R_c , the crystal radius for length; $t_0 = R_c/u_0$ for time; $u_0 = \nu\sqrt{Gr}/R_c$ for the velocity and $\theta = (T - T_0)/\Delta T$ for temperature, where ν is the viscosity, $\Delta T = T_{max} - T_0$, T_{max} is the maximum temperature in the melt and T_0 is the melting temperature of Ge.

The non-dimensional parameters Grashof (Gr), Prandtl (Pr), Schmidt (Sc), Stefan (St) and Peclet (Pe) numbers are defined as:

$$Gr = \beta_T g R_c^3 \Delta T / \nu^2, Pr = \nu / \chi_L, Sc = \nu / D_L, St = \gamma \rho_s / (\rho_L c_{pL} \Delta T), Pe = Pr \sqrt{Gr}, Pe_d = Sc \sqrt{Gr}$$

where β_T is the coefficient of volumetric expansion, g is the gravitational acceleration, χ_L is the thermal diffusivity of the melt, and D is the diffusion coefficient. Thermal conductivity λ , specific heat c_p , density ρ are non-dimensionalized by their value in the melt $\lambda_L, c_{pL}, \rho_L$,

$$\bar{\lambda} = \lambda / \lambda_L, \bar{c}_p = c_p / c_{pL}, \bar{\rho} = \rho / \rho_L.$$

In the region C_1 (see Fig. 3), the Navier-Stokes equations for an incompressible viscous liquid, in which the Boussinesq approximation is applied, may be written in vorticity-stream function form as:

$$\frac{\partial \omega}{\partial t} + D(\psi) \omega = \frac{1}{Re} \frac{1}{r} \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial r^2 \omega}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{1}{r} \frac{\partial r^2 \omega}{\partial z} \right) \right] + \frac{Gr}{Re^2} \frac{1}{r} \frac{\partial T}{\partial r}$$

and $\frac{1}{r} \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \psi}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{1}{r} \frac{\partial \psi}{\partial z} \right) \right] + \omega = 0$ in which the stream function and vorticity are defined as

$$u = \frac{1}{r} \frac{\partial \psi}{\partial z}, w = \frac{1}{r} \frac{\partial \psi}{\partial r}, \text{ and } \omega = \frac{\zeta}{r} = \frac{1}{r} \left(\frac{\partial w}{\partial r} - \frac{\partial u}{\partial z} \right)$$

The equations for heat and mass transfer are solved in the region C_1

$$\frac{\partial T}{\partial t} + D(\psi) T = \frac{1}{Pe} \nabla^2 T, \quad \frac{\partial c}{\partial t} + D(\psi) c = \frac{1}{Pe_d} \nabla^2 c$$

In the above equations, the operator for the convective terms ($\phi = \omega, T, c$) is defined as

$$D(\psi) \phi = \frac{1}{r} \frac{\partial}{\partial r} \left(\frac{\partial \psi}{\partial z} \phi \right) - \frac{1}{r} \frac{\partial}{\partial z} \left(\frac{\partial \psi}{\partial r} \phi \right).$$

The equation for heat conduction is considered within the area occupied by the crystal and crucible walls:

$$\bar{c}_p \bar{\rho} \frac{\partial T}{\partial t} = \frac{1}{Pe} \nabla \cdot (\bar{\lambda} \nabla T)$$

Time dependent experimentally measured temperatures were imposed at the external boundary of the crucible, at the baffle heater and gap δ between the baffle heater and crucible wall. These transient values were recorded at the thermocouple locations; the temperature between these points was determined using interpolation techniques. The discontinuity of the properties λ, c_p and ρ and continuity of the heat flow are imposed at the crystal-crucible and melt-crucible boundaries:

$$[T] = 0, \quad \left[\frac{\bar{\lambda}}{Pe} \frac{\partial T}{\partial n} \right] = 0.$$

Here and below, $[]$ denotes the change of the function inside the brackets across the interface. A symmetry condition is imposed at the axis for both temperature and velocity. The normal component of the velocity

of the melt-solid interface, V_{n_z} , is determined at each time step from the Stefan condition

$$T = T_0, \quad \left[\frac{\bar{\lambda}}{Pe} \frac{\partial T}{\partial n_z} \right] + St V_{n_z} = 0,$$

where T_0 is the temperature at which phase change occurs. The vertical component of velocity at the inflow region (see Fig. 3) is determined from a mass balance, viz.:

$$V_{\delta} = -V \frac{R_h^2}{I - R_h^2}$$

where R_h is the radius of the baffle heater. The imposed stream function conditions on the top melt boundary therefore become:

$$\begin{aligned} \psi &= -V \frac{r^2}{2} \text{ for } 0 < r < R_h, \quad \frac{1}{r} \frac{\partial \psi}{\partial n} = 0 \text{ for } 0 < r < I, \\ \psi &= -V \frac{R_h^2}{2} + \frac{r^2 - R_h^2}{2} \frac{V R_h^2}{I - R_h^2} \text{ at } R_h < r < I \end{aligned}$$

On the phase change boundary and on the side surface of the melt: $\psi = 0, \quad \frac{1}{r} \frac{\partial \psi}{\partial n} = 0$

A symmetry condition for the concentration is imposed along the axis and a zero concentration flux set on the crucible wall and heater. The condition of the balance for the concentration flux and dependence of concentration in the solid and the liquid phases is determined by an equilibrium condition at the interface

$\frac{1}{Pe} \frac{\partial c}{\partial n_z} + V_{n_z} c = V_{n_z} c_s, \quad c_s - k_0 c$, in which k_0 is the partition coefficient. A mass balance condition is used

at the inflow region: $\frac{1}{Pe_d} \frac{\partial c}{\partial z} + (V - V_{\delta})c = (V - V_{\delta})c_2$

where c_2 is the concentration in Region C_2 . It is assumed that above the baffle heater, in C_2 (see Fig. 1), the melt is well mixed, and the concentration in this zone is time independent. The initial temperature distribution is set to $T(z) = T_0$ for the whole calculation domain. The initial melt velocity was set to zero.

Results

Sample Grown with the AHP Unit-1

Only one crystal was grown with the unit that used a graphite baffle with a heater encased in it. This crystal is designated as Sample I. Figure 4 shows the etched half of the crystal along with a schematic of its features, denoting the single and polycrystalline regions. The crystal was grown at 20 mm/h pulling rate. During the growth up to 25 mm, the crystal was melted back and regrown a couple of times by adjusting the temperature of the baffle to demarcate the s/l interface. Similar melt backs were also done towards the middle and end of the sample. Experimental temperature profiles show these thermal fluctuations, Figure 5. Numerical modeling predicted 0.3-0.4 cm/s flow velocity (indicating a well-mixed liquid) and change in the direction of streamlines due to the thermal oscillations, Figure 6. Although, the melt height below the baffle, h , changed in the range 5-20 mm during the melt backs, it stayed almost constant at ~20 mm during the growth (see Fig. 6). Clear striations appeared in the sample delineated the shape of the s/l interface at different times during growth. Convex, concave, and nearly planar interface shapes were observed during the growth depending on the change in the thermal profile around the interface. However, in all interface configurations, deviation from planarity was in the range 1.0-1.7 mm.

Radially averaged longitudinal, measured solute concentration data for Sample I is plotted in Figure 7a with different prediction methods to compare the experimental data with the theoretical predictions. The

upper boundary for solute build up in the AHP grown crystals is given by considering only diffusional mixing in a melt geometry similar to that in floating zone technique²². In contrast, the lower boundary is given by considering the complete mixing in the melt, again similar to floating zone melt geometry¹⁶. The equation describing these two different approaches is essentially the same with a different decay constant:

$$C_s = C_o [1 - (1-k)e^{-\lambda x}]$$

in which $\lambda = (kv/D)(1-e^{-(vh/D)})^{-1}$ for diffusional mixing in the melt and $\lambda = k/h$ for complete mixing in the melt, where C_s is the solute concentration in the solidified crystal, C_o is the initial solute concentration in the melt, k is the partitioning coefficient, v is the growth velocity, D is diffusion coefficient of solute in the melt, h is the melt height, x is the distance solidified, and λ is the decay constant. The plots in Figure 7 were constructed by using these two approaches with $k = 0.003$ and $D = 5 \times 10^{-5} \text{ cm}^2/\text{s}$. The plot in Figure 7a shows that appreciable mixing took place during the growth of Sample I as also predicted by the numerical model. Axial solute concentration data for this sample, obtained via numerical modeling, matched the experimental data fairly well, Figure 8. Radial solute segregation in this sample ranged from 10% to 50% and shown in Figure 9a. In general, whenever the interface was close to planar, the radial segregation was minimal. High radial segregation (50%) was observed during the thermal fluctuations mentioned earlier. Also, comparison of Figure 9 with Figure 4 shows that high points on radial concentration profiles coincide with the low points of the striations appeared in the sample.

Samples Grown with the AHP Unit-2

Four samples were grown with this unit that used a baffle without a heater and a conical insert to facilitate single crystal formation. Two of the four samples, grown at 3 mm/h (Sample II) and 5 mm/h (Sample III), were completely single crystal. The other two samples grown at 10 mm/h (Sample IV) and 20 mm/h (Sample V), on the other hand, displayed columnar growth after a single crystal region. In Sample III, the cellular growth appeared at 22 mm from the top of its conical portion as seen in Figure 10, as compared with only 6 mm in the sample grown at 20 mm/h velocity (Sample V). In both samples, outline of the interface breakdown region resembled the shape of the conical insert.

Axial dopant concentration of the crystals increased smoothly as seen in Figure 7b-e. However, radial solute segregation in the crystals changed depending on the melt height below the baffle and growth velocity, Figure 9b-e. At the beginning, the radial segregation was 20% in Sample II, grown at 3 mm/h. Later, the segregation further increased to about 30% for a short distance and then started decreasing down to 8% at the end of the growth. For this sample, the melt height was initially 9 mm and increased about 75% at the end. On the other hand, Sample III, grown with 5 mm/h velocity, showed about 1.5% radial segregation at the beginning, which progressively increased to 45% at the end of the growth as the melt height decreased 45% from its initial value of 13 mm. Sample IV, grown with 10 mm/h velocity, had 25% radial segregation at the beginning, and it increased to 75% before the interface breakdown occurred. The melt height increased about 15% from its initial value of 13 mm. Radial segregation was already 75% at the beginning of Sample V, grown at 20 mm/h rate. No further data collection was possible for this sample because the interface instability observed at 6 mm above its conical section as stated before. Melt height for this sample increased 50% from 12 mm during the growth.

Discussions

As already stated, the segregation in melt grown crystals is mainly controlled by the interface shape and convection, both of which can be modified by changing the experimental parameters. Reduction in melt height, which is one of the main features of the AHP method, decreases the buoyancy driven convection in molten solutions considerably. This in turn can decrease the radial segregation in growing crystals. The dimensionless Rayleigh (Ra) number describes the convection in molten solutions¹³.

$$Ra = \frac{g\beta G_L h^4}{\alpha v} \sim \frac{\text{buoyancy forces}}{\text{viscous forces}},$$

where g is the gravitational acceleration, β is the coefficient of thermal expansion for melt, G_L is the temperature gradient in the melt, h is the melt height, α is the thermal diffusivity, and v is the kinematic viscosity. For instance, in conventional crystal growth techniques, the initial melt height is usually in the order of 100 mm. However, the AHP technique reduces the melt height to around 10 mm, decreasing the Ra number of the melt by a factor of 10^4 . In our experiments, melt height was kept in the range 5-20 mm. It can be then deduced from the foregoing that in this study, buoyancy driven convection in the melt is lowered.

Although, the AHP method reduces the buoyancy driven convection significantly, it still creates a forced convection in the melt below the baffle by the flow of liquid from the region above the baffle to the region below the baffle (see Figure 1 for melt flow). The potency of the forced convection can be shown by defining a “characteristic ratio” as the ratio of the melt height below the baffle to the length of diffusion boundary layer in front of the growth interface. Length of the diffusion boundary layer is given as $2D/v$, where D is the solute diffusivity in the melt and v is the growth velocity^{23, 24}. Depending on the value of the characteristic ratio, forced convection can appreciably disturb the melt near the s/l interface. The disturbance will be less when the characteristic ratio is larger than 1 and vice versa.

Experimentally determined axial solute concentration data for Sample I, shown in Figure 7a, fall closer to the theoretical data obtained considering complete mixing in the melt. This unexpected observation could be a result of following reasons. The characteristic ratio for the growth of Sample I is in the range 2.77-11.11, indicating that forced convection was weak. However, the temperature fluctuations during the interface demarcations might have caused buoyancy driven convection that stirred the melt. Numerical model that used the experimental thermal data at the boundaries also predicted about 0.3-0.4 cm/s flow velocity, indicating a well mixed melt below the baffle. However, in spite of the convection (buoyancy and/or forced), the axial heat supplied by the heater in the baffle kept the s/l interface mostly planar, parallel to the base of the baffle. As seen in Figure 4, the deviation of the s/l interface from planarity is only 1.7 mm at the beginning and 1 mm later on. The planar interface also reflected itself in the plots of radial concentration data for Sample I, Figure 9a. In general, the radial segregation was about 10%, except for the 50% segregation observed at the beginning (14 mm from the seed base) where temperature fluctuations took place. Hence, so long as the interface is kept planar by axial heat supply, convection is not able to create radial segregation.

It was observed that the distance to interface breakdown depended on the initial solute concentration in the melt and the growth velocity, Table I. Two samples grown with 3 mm/h (Sample II) and 5 mm/h (Sample III) did not display any interface instability because apparently there was not enough solute build up at the interface to render the interface unstable due to their low growth velocity. On the other hand, the other

3 samples showed instability at different distances depending on their initial solute concentration and the growth velocity. The interface in Sample IV, grown at 10 mm/h velocity, became unstable after 22 mm. Sample V, grown at 20 mm/h rate, had the same initial solute concentration as in Sample IV; however, it went unstable only after 6 mm because of its higher growth velocity. In contrast, interface breakdown in Sample I, grown with 20 mm/h velocity using the AHP Unit-1 with a heater in the baffle, occurred at a longer length (72 mm) than that in Sample V, which was also grown with 20 mm/h velocity. This was partially because Sample I had a lower initial solute concentration, see Table I. Another reason for this observation may be the kinetic stability due to having a planar interface in Sample I.

Although Figure 7 indicates that all samples experienced a considerable amount of convection during growth, resemblance of the outline of the cellular region in Sample IV and Sample V to the shape of the conical insert can be evidence to the absence of complete mixing in the melt. If there had been a complete mixing, since the concentration everywhere in the melt would have been the same, shape of the interface breakdown would not have conformed to the shape of the insert.

It should be noted that the conical graphite insert is expected to significantly change the thermal profiles in the growing crystal. This is particularly significant for the present experiments, since the thermal conductivity of graphite is about 5 times larger than that of solid Ge. Thermal calculations will be conducted to incorporate the influence of the insert on the temperature fields and consequently the shape of the interface.

Conclusions

The AHP method uses an axial baffle with or without a heater in it. The baffle effectively reduces the melt height and consequently the buoyancy driven convection in the melt. However, the AHP method still creates a forced convection in the melt below the baffle. The experimental observations suggest that regardless of the growth velocity and perhaps the melt height, a planar growth interface can be achieved with the AHP method by use of a heating element in the baffle that is positioned near the s/l interface and supplies heat axially to it. This is because, in addition to supplying heat axially to the interface, the axial heater also homogeneously distributes the heat evenly over the growth interface. Thus, the baffle with heater forces the interface stay planar. On the contrary, a choice of proper melt height and efficient heat removal from the interface through the growing crystal seem to be important to keep the s/l interface planar during the growth from the melt by the AHP method without a heater in the baffle. By achieving a planar interface either way reduces the radial dopant segregation.

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Table I. Experimental parameters, cell incubation distance, and characteristic ratio.

Sample Number	C_o , ats. Sb/cc	v , mm/h	G_L , °C/cm	h , mm	Measured Cell incubation Distance, mm	$2D/v$, mm ($D=5 \times 10^{-5}$ cm^2/s)	Characteristic ratio = [$h/(2D/v)$]
I	5×10^{19}	20	10	5-20	72	1.8	2.77-11.11
II	5×10^{19}	3	17-10	9-16	No cells	12	0.75-1.33
III	1.10×10^{20}	5	6-7	13-7	No cells	7.2	1.8-0.97
IV	1.47×10^{20}	10	6-7	13-15	22	3.6	3.6-4.16
V	1.47×10^{20}	20	9-8	12-18	6	1.8	6.6-10

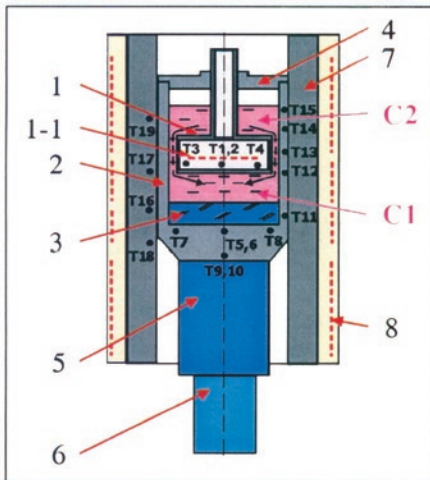


Figure 1. Schematic of the AHP Unit-1. The unit uses an axial baffle with a heater encased in it. Arrows around the baffle show the melt flow during the growth.

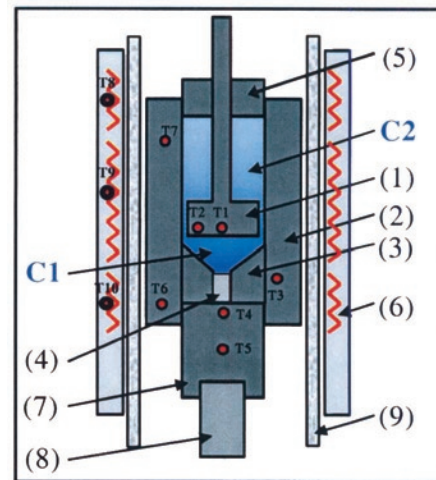


Figure 2. Schematic of the AHP Unit-2. The unit uses an axial baffle without a heater.

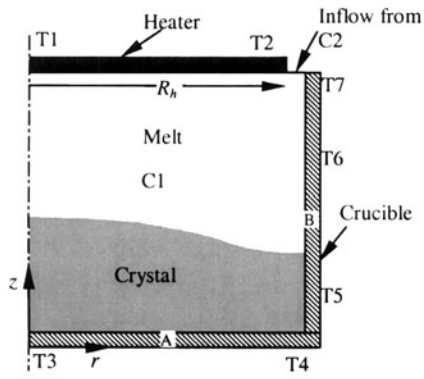


Figure 3. Computational domain.

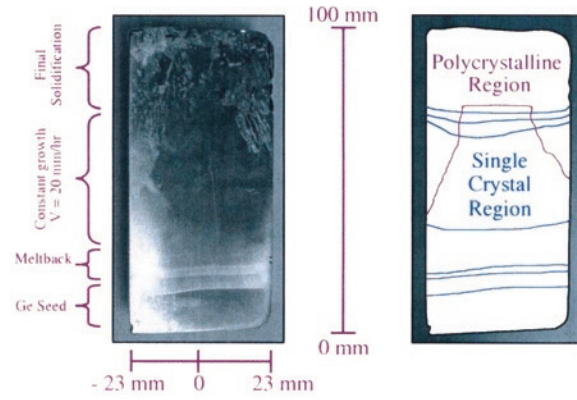


Figure 4. Sample I grown with the AHP Unit-1. Single, polycrystalline, and meltback regions are shown in the original photo and the schematic.

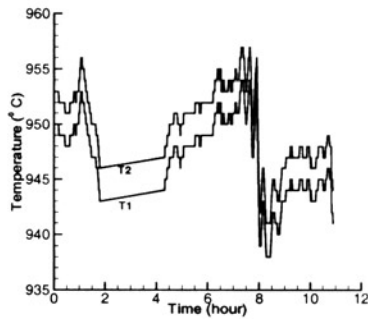


Figure 5. Thermal profile on the baffle (Thermocouples T1 and T2). Growth took place between 4.5th and 7th hours.

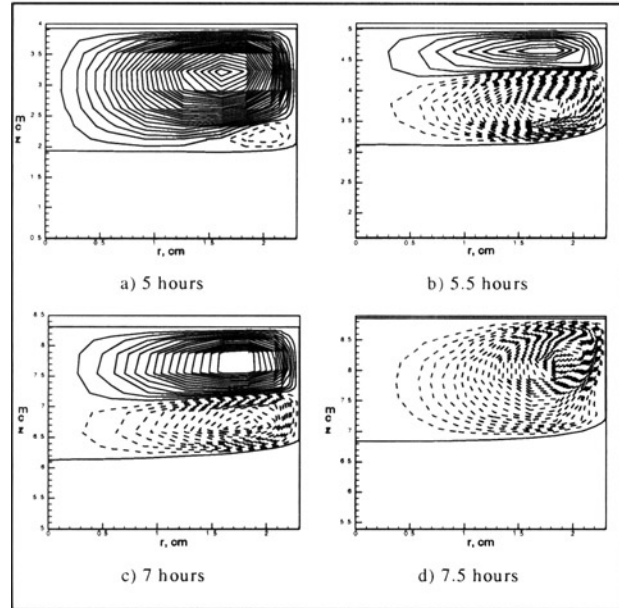


Figure 6. Stream functions during growth of Sample I. Dashed lines show the negative flow direction.

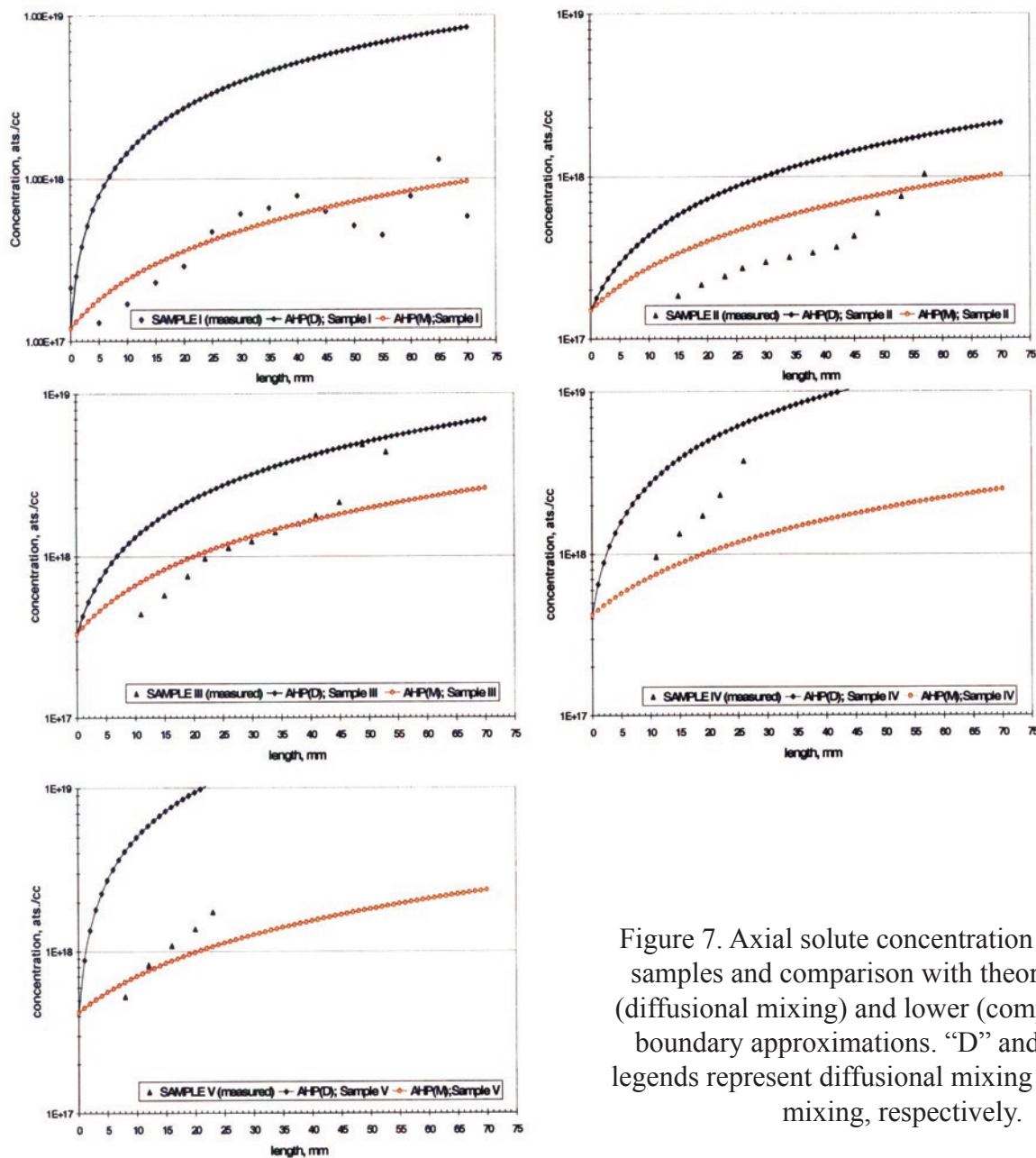


Figure 7. Axial solute concentration in the grown samples and comparison with theoretical upper (diffusional mixing) and lower (complete mixing) boundary approximations. “D” and “M” in the legends represent diffusional mixing and complete mixing, respectively.

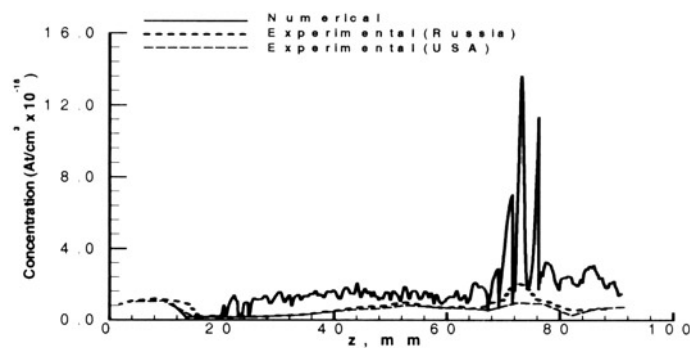


Figure 8. Axial solute distribution in Sample I, predicted by the 2-D numerical model and measured in two different laboratories in MSE-UF/USA and Russia.

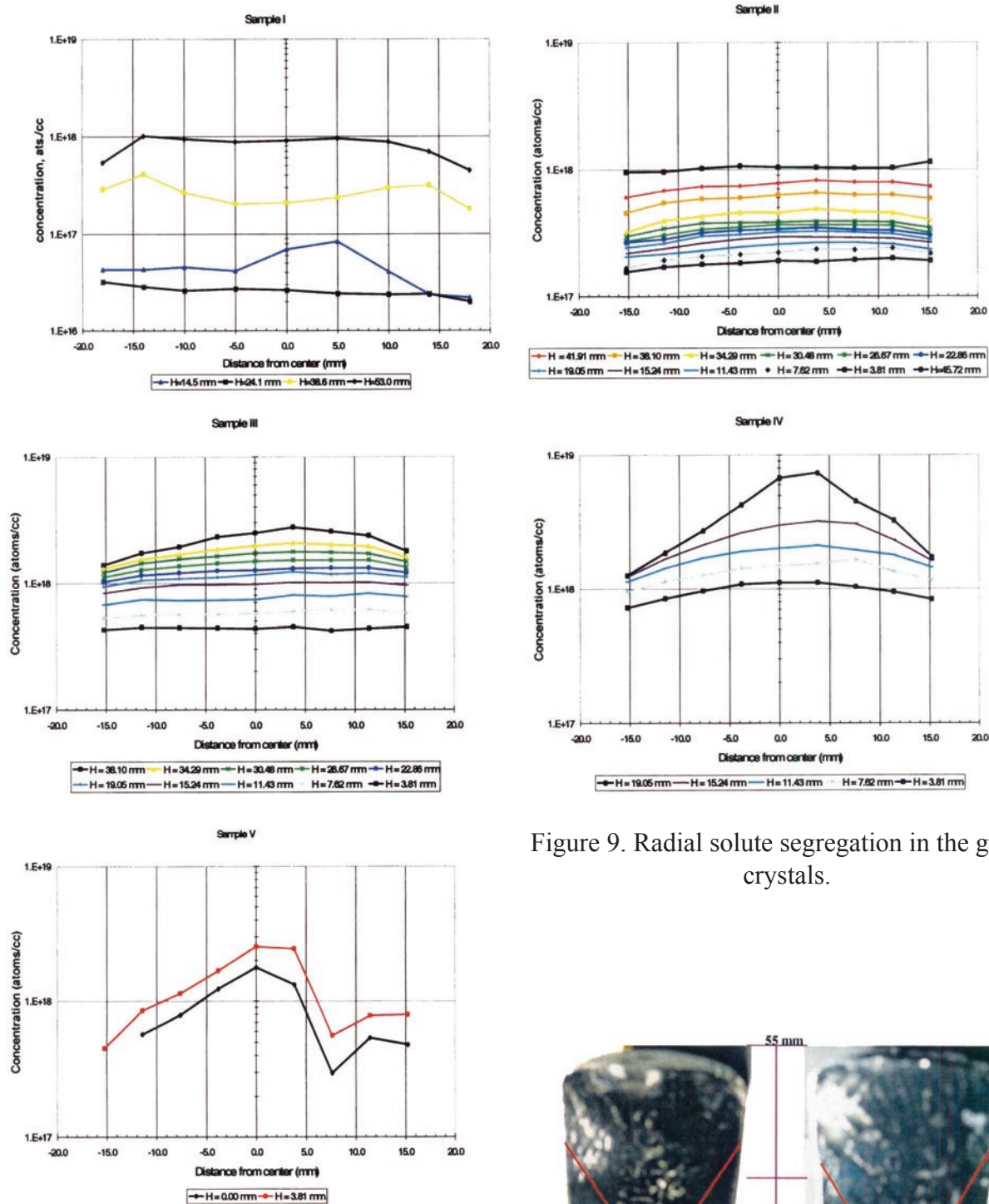


Figure 9. Radial solute segregation in the grown crystals.

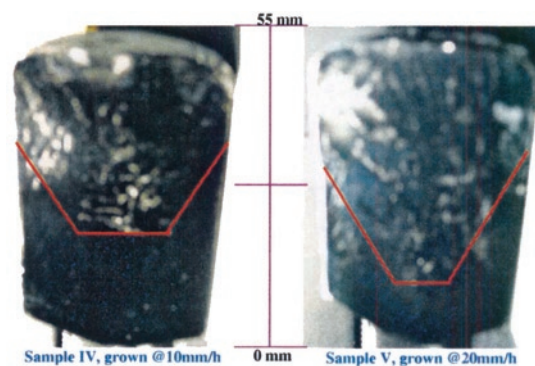


Figure 10. Interface breakdown in Sample IV and V. Outline of the breakdown resembles the shape of the conical insert.

VIBRATIONS AND G-JITTER: TRANSPORT DISTURBANCES DUE TO RESIDUAL ACCELERATION DURING LOW GRAVITY DIRECTIONAL SOLIDIFICATION EXPERIMENTS

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Abstract

This research project is a four-year program of ground-based research. The proposed work involves both experimental and theoretical (numerical modeling) work. The experimental objectives are to characterize the response of heat and species transport in a directionally solidifying two-component melts (for both single and two-phase liquids) that are subject to well-characterized imposed vibrations and to spacecraft residual acceleration. The experimental work will focus on the examination of flow induced by applied vibration, (both uniform translational vibration and nonuniform vibration) and the consequences of this flow for heat and mass transport. To start we are restricting our investigation to simple systems and plan to extend our investigation to solidifying model alloys system during the last half of the program. The planned solidification experiments will use succinonitrile (SCN)-Water or SCN-Ethanol as a model alloy system. The temperature and composition fields will be measured using two-color holographic interferometry to characterize the composition and temperature fields. The convective flows will be visualized using a schlieren technique and selected experiments will involve Particle Image Velocimetry.

For numerical modeling, for single-phase systems, we use the Navier-Stokes-Boussinesq equations for single-phase systems and the so-called “Thermovibrational” average equations for uniform and nonuniform vibration to investigate the role of vibration-induced mean flows. For two-liquid phase melts (for example, that occur in monotectics systems), we are exploring the possibility of using a Lattice Boltzmann approach.

In this report, we discuss preliminary results for the generation of mean flows by vibration and effects on heat and mass transfer for microgravity and 1- g conditions. Mean flows caused by high frequency vibration are found by time averages of numerical simulations of the Navier-Stokes (NS) equations and from the thermovibrational mean flow equations developed by Gershuni et al. [1]. A quantitative investigation is carried out. Comparisons of time-averaged NS and the Gershuni equations are made for a wide range of parameters. The conditions for which the Gershuni equations should yield reliable predictions are explored. Based on the assumptions used to obtain the thermovibrational mean flow equations, the thermovibrational equations are valid when $\sqrt{2PrRa_v}/\Omega \ll 1$. Here, $\Omega = \omega L^2/\alpha$ is a dimensionless frequency and $Ra_v = (b\omega\Delta TL)^2/2\nu\alpha$ is the vibrational Rayleigh number, and ω , L , b , ΔT , ν and α are the vibration amplitude, the length of the container, the vibration amplitude, the characteristic temperature difference, the kinematic viscosity and the thermal diffusivity, respectively.

Keywords: g-jitter, meanflows, transport, directional solidification, thermovibration

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In addition to the numerical modeling work, experimental work on the response of flow and transport to vibration is in progress. The experimental set-up is described and planned experiments are discussed.

Objectives and motivation

The objectives of this research are:

- To examine, characterize and quantify the relative effects of linear translational vibration and non-uniform vibration on transport in directional solidification experiments under low gravity conditions.
- To investigate, through experiments, the effects of residual acceleration (g-jitter) on fluid motion and heat and species transport during directional solidification experiments for single and two-phase.

The specific aims are:

- Investigation of mean flows due to high frequency vibration
- Explore differences between ‘first’ and ‘second’ order thermovibrational mechanisms (nonuniform and uniform vibration) using numerical models and through experiments
- Investigation of the interaction between thermal and solutal buoyancy in the development of mean ‘thermovibrational’ flows
- Experimentally investigate the effect of vibration on melts with two liquid phases (monotectics)
- Develop an approach for simulation of thermovibrational flow and transport in with two liquid phases (monotectics)

The sensitivity of crystal growth experiments is well understood insofar as the effects of uniform single-axis translational vibration on thermal buoyancy-driven convection are concerned. However, the response of systems with strong dependence of density on temperature and concentration has not been so well studied. A comprehensive study of transport response to general vibrations with both translational and rotational components is also needed. In all cases, with the possible exception of impulse disturbances, experimental quantification of model predictions is lacking. The following questions regarding vibration and g-jitter effects on transport during directional solidification of alloys and compound semi-conductors have yet to be adequately addressed:

- What quantitative experimental results exist that demonstrate the response of transport during directional solidification of binary systems to low-frequency g-jitter.
- What is the effect of g-jitter on binary systems that possess an immiscible two-liquid phase region?
- Spacecraft frequently undergo rotational oscillations within a dead-band about their nominal attitude. How is transport in a directionally solidifying alloy affected by these “pendulum-type” oscillations which are known to cause fluid motion even in homogenous contained fluids?
- Does multi-frequency g-jitter with time-dependent magnitudes and orientation result in the generation of mean flow in a manner akin to first-order thermo-vibrational mechanisms?
- Can controlled vibration be used as an effective flow control under low gravity conditions?

Aside from the MEPHISTO flight experiment results [2-6] g-jitter sensitivity studies to date, there are only a few quantitative measurements of g-jitter effects on microgravity experiments. This is a significant omission, particularly given the emphasis on determining “low gravity requirements” for Spacelab experiments and, more recently, space-station redesign. Without experimental calibration or verification, model predictions are of limited use. Since it is possible to check model predictions through carefully planned experiments there is no reason to let such uncertainty persist. The g-jitter experiments carried out

on MEPHISTO yielded valuable information about experiment response to g-jitter. Yet more information is needed on the effects of background g-jitter, multi-frequency disturbances and rotational vibrations. Experiments with well-defined applied oscillatory vibration are needed not only for g-jitter sensitivity assessment, but also to investigate the possibilities of using vibration for transport control (for example for melt homogenization or rehomogenization).

Significance

The design of experiment facilities and planning of specific experiments for the International Space Station and other orbital platforms requires that the experiment's sensitivity to microgravity residual acceleration be assessed. Residual acceleration arises due to transient and vibrational disturbances (g-jitter), atmospheric drag on the spacecraft and the gravity gradient. The interaction of residual acceleration with density gradients in fluids will generally produce buoyancy driven flows within those fluids. Experiments involving fluids with density gradients are conducted in low gravity so that buoyant convective motion that is unavoidable under terrestrial conditions is reduced or eliminated. To make best use of the available experiment time and to eliminate any ambiguities in the interpretation of experiment results it is therefore essential to assess the sensitivity of a given experiment to time-dependent and steady acceleration. To date, nearly all the work that addresses the impact of residual acceleration on low-gravity experiments relies on the results of numerical modeling and scaling analyses. Experimental quantification or verification is all but lacking. On the other hand, questions regarding the possible influence of residual acceleration effects on actual flight experiments still persist. The recent MEPHISTO flight experiments (conducted on USMP-3, in February-March 1996) were the first experiments to be conducted to characterize the effects of impulse disturbances (caused by thruster firings) on transport during directional solidification. The experiment results clearly demonstrated the ability of numerical models to predict the convective transport response to impulse disturbances. However, a quantitative characterization of experiment response to other forms of g-jitter acceleration is still lacking, most notably in the area of vibration and rotational acceleration. (Note that for rotational accelerations that involve "pendulum" or rocking type motions, fluid motion can occur *even in the absence of density gradients*). Without quantitative experimental verification, model predictions of experiment response to g-jitter are of limited use and could lead to unnecessary design restrictions or unsuitable experiment operating conditions. Thus, to further improve our ability to predict the impact of vibration and rotational g-jitter acceleration, quantitative experimental data is needed. This will establish a set of benchmark results that can be used to unambiguously define the response of a well-characterized solidification experiment to residual acceleration.

Aside from the possible undesirable responses of transport conditions to uncontrolled g-jitter, it is possible to use *controlled vibration* to provide flows that are tailored to particular crystal growth experiments. These flows would not be accessible under terrestrial conditions due to strong natural convection effects. The microgravity relevance of the proposed work is well established.

Background

It has been known for some time that low-earth laboratories are not characterized by zero-gravity conditions [7-9]. Rather, objects that are capable of independent motion experience acceleration relative to the spacecraft. This acceleration arises from a number of sources and is composed of steady, transient, low (orbital frequencies $\sim 1.8 \times 10^{-4}$ Hz) and high frequency components. Many experimenters seek to use the microgravity environment to avoid unwanted effects of buoyancy as experienced under terrestrial conditions. As a result, there has been considerable interest in identifying and modeling residual

acceleration effects on transport in directional solidification systems. Most recently, this interest has been motivated by the need for

- Acceleration requirements to be used in design considerations
- Quantitative assessment of residual acceleration effects
- Minimization of the impact of residual acceleration through an optimal choice of experiment operating conditions

Thus, there are a number of papers that examine the effects of residual acceleration (for reviews see [10-13]). The most studied g-jitter problems are those involving the prediction of solute redistribution during the directional solidification of binary alloys and compound semiconductors [2,3, 14-16]. The possibility that steady acceleration can be reduced by factors of 10^6 or more in comparison to terrestrial conditions suggests that buoyant melt convection, which might lead to undesirable levels of compositional nonuniformity, can be sufficiently reduced to allow diffusive conditions to prevail. It then follows that, assuming an initially uniform melt, lateral or radial compositional nonuniformity would arise only when the crystal-melt interface exhibits significant deviations from planarity. However, early studies, based on scaling and analytical models, predicted that even with a reduction to $10^{-6}g$, a steady acceleration could result in sufficient convection to cause significant lateral nonuniformity. This has been confirmed by numerical simulation [3,17]. Time dependent residual acceleration has also been examined. The effects of impulse disturbances were recently characterized through a series of experiments conducted with a directional solidifying alloy on USMP-3 although analysis has generally been restricted to single frequency sinusoidal acceleration disturbances that correspond to oscillatory translational displacements of the ampoule-melt system (see, for example, [4,15,16, 17]). Some analyses have used actual acceleration time histories measured using NASA's Space Acceleration Measurement System (SAMS) [15,18], but were restricted to rectilinear acceleration (i.e., corresponding to rectilinear translational vibrations). From these, and other studies of the effects of oscillatory acceleration, it appears that the 'solutal' cut-off frequency [6] is extremely low for most solidification experiment operating conditions. This means that the higher frequency g-jitter should have a negligible impact on solute segregation compared to quasi-steady accelerations. However, these analyses have not accounted for rotational acceleration, nor do they address the possibility of mean flow generation.

Thermovibrational convection

Most studies of thermovibrational mean flows that are pertinent to solidification scenarios have involved a consideration of completely contained fluids; moreover, the orientation of the rigid container is held fixed. For this particular case (i.e., for uniform vibrations), the nonuniformity of the density and the pulsating velocity field are proportional to a (small) parameter $\varepsilon = \beta\theta$. In this case, the thermovibrational effect is of second order with respect to ε . For a nonisothermal fluid subject to nonuniform vibration it can be shown [19-22] that for a weak dependence of the density on temperature, the nonuniform pulsating velocity field is independent of the thermal conditions and the effective vibrational body force is linear in $\varepsilon = \beta\theta$. Thus, for nonuniform vibrations, the thermovibrational effect (i.e., the mean flow) is of first rather than second order. Mean flows produced by first order thermovibrational mechanisms have been examined for several special cases including the oscillations of a heated sphere [23,24]. Examples of nonuniform vibration include non-translational vibrations of a solid body immersed in a fluid, vibrations of partly filled containers, layered immiscible fluids, or vibrations of elastic containers. In addition to mean flows generated by first and second order thermovibrational mechanisms, mean flows can be generated by nonuniform vibration in *homogenous* fluids by through the Schlichting mechanism [19,25,26].

Most recently, in the context of g-jitter on ISS, Savino [27] has examined thermovibrational mean flow (modified to include solutal buoyancy) effects on transport during 1) measurement of the thermal conductivity in high Prandtl number liquids; 2) measurement of the thermodiffusion coefficient in binary mixtures. His results showed that, for the microgravity environment of the ISS, the NSB and Thermovibrational formulations gave almost the same results. Simulations at different orientations of the residual-g and g-jitter show that, orienting the residual-g parallel to the density gradient, reduces the convective disturbances and can also help mitigating the disturbances induced by the g-jitter.

Stochastic g-jitter

Time-dependent and mean flows due to stochastic g-jitter have been examined [28,29]. A stochastic description of the residual acceleration field onboard spacecraft (g-jitter) was developed [28,30] to describe in quantitative detail its effect on fluid motion. The main idea behind their approach is that such a statistical description is necessary in those cases for which characteristic time scales of the process are long compared with the correlation time of g-jitter. There are a few difficulties with this approach. Firstly, the g-jitter time series are not statistically stationary but have definite dependencies on factors such as active rest crew periods, dithering of antennae and other specific activities where machinery may induce vibrations of a particular frequency and amplitude for sustained time periods. Furthermore, it is difficult to extract the low frequency range of the microgravity acceleration power spectrum. This range controls the magnitude of diffusive processes. Finally, models used to date are Gaussian, but there is evidence that the frequency with which large amplitude disturbances occur is higher than a Gaussian model would predict [28]. For a randomly vibrating plate in a fluid, it was found that the vorticity decayed as a power law away from the boundary, even if the average vorticity production was zero. In contrast, periodic motion with zero average vorticity production results in an exponential decay of the vorticity away from the boundary.

Vibration as a method of flow and transport control.

For vibrations with specially chosen axes, the natural buoyancy driven convection, which prevails in the absence of vibration, can be suppressed at certain frequencies and amplitudes [31]. This has recently been analyzed in more detail [32] using the full equations of motion and also the time-averaged equations from [33]. The possibility of using vibration as a means of controlling and suppressing convection was confirmed (See also Fig. 1, showing the dependence of the average Nusselt number on the thermovibrational Rayleigh Number $Rv = (\Omega b \beta \theta L)^2 / 2\nu\kappa$ [33,19-22]. Here β , ν , and κ are, respectively, the fluid's thermal expansion coefficient, kinematic viscosity and thermal diffusivity, and θ is the characteristic temperature difference of the system. A comprehensive introduction to vibrational convection and other problems associated with time-dependent modulation of boundary conditions can be found in references [19,33]. There are several examples of experimental work concerning the influence of vibration on crystal growth from melts and solutions [34-44]. These works involved a wide range in intensities and frequencies (including ultrasound). Experimental attempts to understand how low frequency vibrational stirring might be used to effect rapid mixing in melts and solutions have been made by Liu et al. [40]. The influence of low frequency vibration on interface location and shape during Bridgman growth of cadmium telluride was examined by Lu et al. [41]. Other effects of low frequency vibrational convection on crystal growth include the increase in local perfection of binary compound semiconductors [42], changes in interface shape [43], and the faceting of germanium crystals [44]. The elimination of striations in indium antimonide may also be due to the formation of a stationary melt flow due to torsional vibration [45]. Experimental results also clearly show that in certain cases vibrational convection can provide enhanced nutrient fluxes during the solution

growth of Rochelle salt and potassium dihydrogen phosphate (KDP) [46,47]. Zharikov [48] identified a characteristic low frequency (< 100 Hz) vibrational flow regime in the liquid near a growing crystal. The form, dimensionality and intensity of the flow were studied and the effects of vibration on heat and mass transfer were analyzed for the case of Czochralski and Bridgman growth of sodium nitrate (NaNO_3). He showed that the vibration could drastically alter the character of flow and concluded that vibration could exert a strong influence on transport, and impurity incorporation and locally influence growth kinetics.

More recently, mean flow and vibration for flow flow control in crystal growth systems has been examined by Lyubimov *et al.*, [49] and Fedoseyev and Alexander [50]. In the former work, the coupling between the three basic mechanisms of flow generation induced by vibrations (Schlichting mechanism, surface-wave mechanism, and thermovibrational mechanism) is examined. The conditions under which vibration-induced flows can be used to efficiently control heat/mass transfer during real industrial applications of crystal growth from the liquid phase, by counteracting buoyancy- and/or thermocapillary-driven flows were discussed.

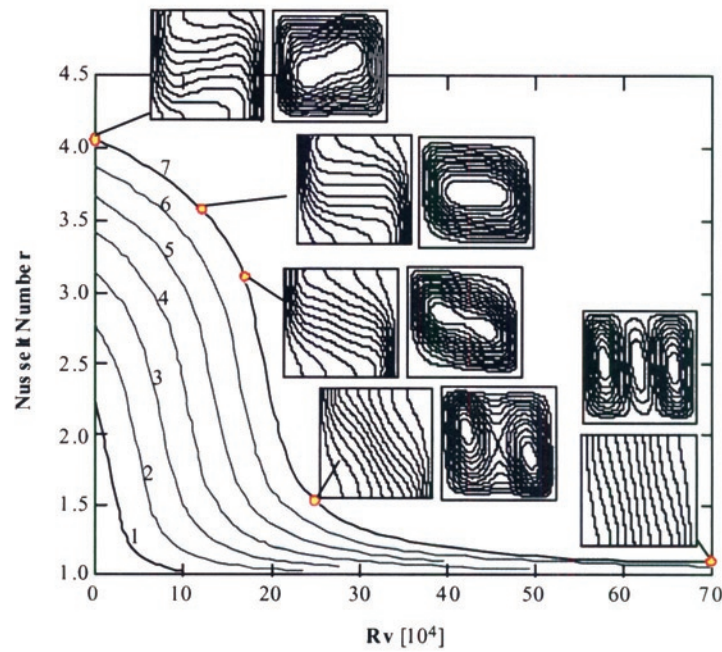


Fig. 1 Mean Nusselt number vs. vibrational Rayleigh number for high frequency thermovibrational convection [31,52]. Mean streamlines and isotherms are inset. Numbers on curves are the values of the steady Rayleigh number.

Uspenskii and Favier [51] considered the interaction between high frequency and natural convection in Bridgman-type crystal growth. They used the average thermovibrational flow equations to theoretically examined the problem of suppressing natural convection using high frequency ($\sim 10^4$ Hz) low amplitude vibration and compared the efficiency of vibrational damping to that of magnetic field damping. Using the physical properties representative of GaSb, GaAs, etc., they found that under terrestrial conditions, (for high electroconductivities) the magnetic field is more effective than vibration in damping flow in the horizontal Bridgman configuration. In contrast, for vertical Bridgman, lateral vibration was most effective. The horizontal velocity decreased by a factor of 10 and the vertical velocity by about 20. In

comparison, a 1 Tesla vertical magnetic field only resulted in a factor of 6 decrease in maximum velocity. They speculated that it might be possible to combine magnetic fields with vibration to reach optimal damping conditions.

Progress to date

Numerical simulations

In addition, to exploring g-sensitivity, the use of mean flow generated by vibration to control convection under microgravity conditions is examined. The motivation for this is practical. Low gravity experiments requiring melt-homogenization prior to solidification have no significant buoyant flow to vigorously mix the melt. Even in the event that g-jitter produces “significant” flows, these flows will typically be on the same order as diffusive transport rates. This, given typical experiment dimensions, the time taken to homogenize or rehomogenize a multi-component melt will be on the order of L^2/D where L is the dimension over which the inhomogeneity occurs and D is the diffusivity. These mixing times can be quite long and may result in inhomogeneous initial melt compositions. To study the use of mean flows caused by high frequency vibration we will carry out time averages of numerical simulations using the Navier-Stokes-Boussinesq (N-S-B) equations, as well as using the thermo-vibrational mean flow equations. If mean flow equations can be used to reliably predict the streaming flows resulting from high frequency, low amplitude vibration, they will be a useful for predicting optimum vibration conditions for low-gravity mixing and other situations where flow control is required in low gravity. The nature of these equations is outlined below and we present preliminary results for simple cases with thermally driven vibrational flow. This work is a precursor to a parametric study of mean flow and transport in models of directionally solidifying alloys.

Governing Equations

The dimensionless N-S-B equations for the transport of momentum, heat, and mass take the form

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = \quad (1)$$

$$-\nabla p + Pr \nabla^2 \mathbf{u} - (RaPrT - RasPrC) \mathbf{k} + \Omega \left(\sqrt{2RavPrT} \cos(\Omega t) + \sqrt{2RsPrC} \right) \mathbf{n},$$

$$\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T = \nabla^2 T, \quad \frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = \frac{Pr}{Sc} \nabla^2 C, \quad \nabla \cdot \mathbf{u} = 0 \quad (2)$$

$$\nabla \cdot \mathbf{v} = 0 \quad (3)$$

Here Ra , Ras , Pr , Sc , Rav , Rs , and Ω are the thermal and solutal Rayleigh, Prandtl, Schmidt, thermal and solutal vibrational Rayleigh numbers and dimensionless frequency, respectively. They are given by

$$Pr = \frac{\nu}{\kappa}, \quad Ra = \frac{\beta \Delta T g L^3}{\nu \kappa}, \quad Ras = \frac{\beta_c C_\infty g L^3}{\nu \kappa}, \quad (4)$$

$$Rav = \frac{(\beta \Delta T b \omega L)^2}{2 \nu \kappa}, \quad Rs = \frac{(\beta_c C_\infty b \omega L)^2}{2 \nu \kappa}, \quad \Omega = \frac{\omega L^2}{\kappa}$$

where, ν , κ , D , β , β_c , and L are the kinematic viscosity, thermal diffusivity, solute diffusivity, coefficient of thermal expansion, coefficient of solute expansion and characteristic length, respectively. The angular frequency is ω , g is the gravitational acceleration and ΔT , C_∞ , and b are the characteristic temperature difference, the reference solute concentration and the amplitude of the vibrational displacement.

The averaged or ‘thermovibrational’ mean flow equations are

$$\frac{\partial \bar{\mathbf{u}}}{\partial t} + \bar{\mathbf{u}} \cdot \nabla \bar{\mathbf{u}} = \quad (5)$$

$$-\nabla \bar{p} + Pr \nabla^2 \bar{\mathbf{u}} - (Ra Pr \bar{T} - Ra_s Pr \bar{C}) \mathbf{k} + (Ra_v \bar{T} + Ra_s Pr \bar{C}) (\mathbf{w} \cdot \nabla) (T \mathbf{n} - \mathbf{w})$$

$$\nabla \cdot \bar{\mathbf{u}} = 0, \nabla \cdot \mathbf{w} = 0, \quad \nabla \times \mathbf{w} = \nabla T \times \mathbf{n}, \quad (6)$$

Here $\mathbf{w}$ is the spatially dependent amplitude of the pulsating velocity field and $\mathbf{n}$ is the vibration direction. Note that these equations do not depend on the dimensionless vibration frequency Ω .

Preliminary results: comparison of the mean flow equations with the time-averaged Navier Stokes equations.

Extensive calculations comparing the time averaged Navier Stokes equations with the ‘Thermovibrational’ equations have been carried out. Selected results are shown in Figs. 2 and 3. As predicted by scaling, there is reasonable agreement between them whenever $\sqrt{2 Pr Ra_v} / \Omega \ll 1$.

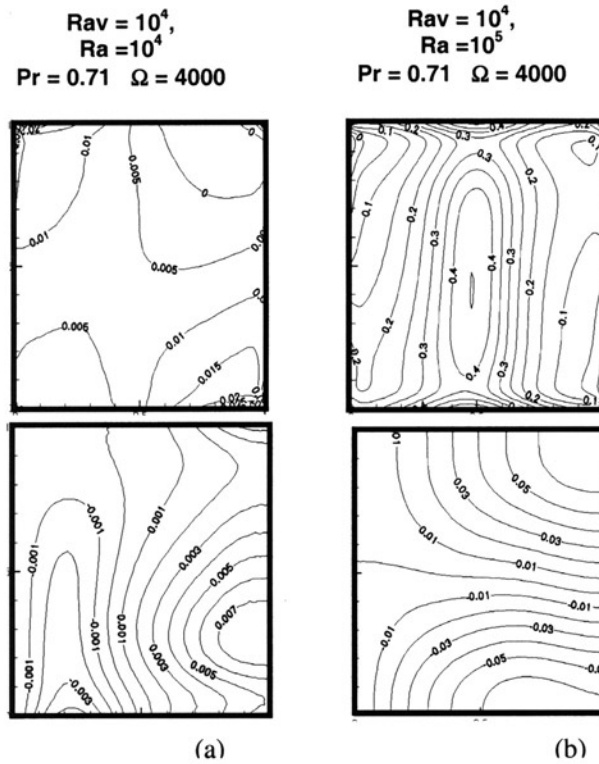


Figure 2. Streamline differences $|(\bar{\psi}_{NS} - \bar{\psi}_{TV}) / \bar{\psi}_{NS}|$ (a) and temperature differences $|(\bar{T}_{NS} - \bar{T}_{TV}) / \bar{T}_{NS}|$ (b) for $\Omega = 4000$.

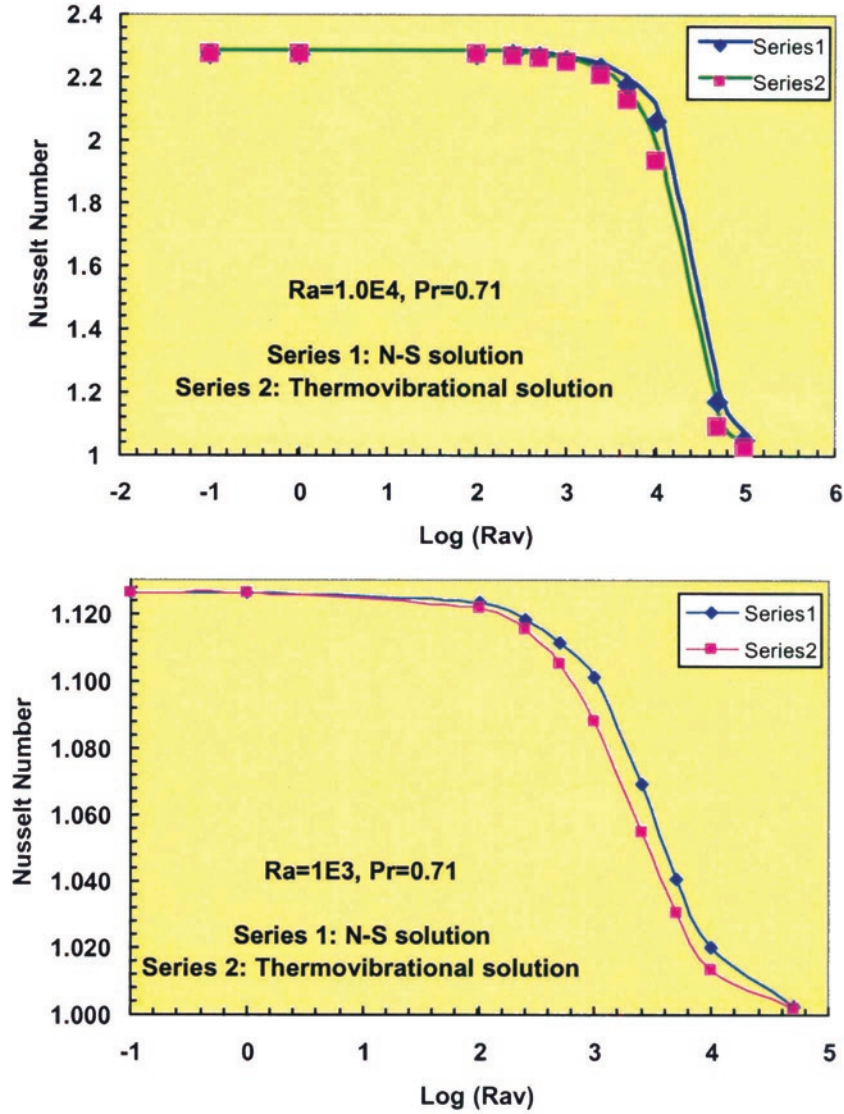


Figure 3. Flow suppression through vibration for $\sqrt{2 Pr Ra_v} / \Omega \ll 1$.

Work in progress and planned work

Work in progress includes:

- Analysis of vibrational effects on transport during directional solidification through numerical simulation using the NSB equations and the ‘Thermovibrational’ equations modified to include solutal buoyancy.
- Analysis of first order thermovibrational effects due to nonuniform vibrations, comparison of Lyubimov’s thermovibrational equations with time-averaged Navier-Stokes-Boussinesq equations.

To investigate the effect of vibration on transport during solidification we have set up a vibration system consisting of a 225 N Shaker with a 1.2 m peak displacement and an operating range of 1 – 7000 Hz. The system is capable of horizontal and vertical translational vibration and specific vibration sequences (Sine wave, random, etc.,) can be programmed and applied to any test cell. For horizontal vibration, test cells

are mounted on a slip table. We have completed preliminary tests of the system and the visualization set-up using silicone oils in open tall narrow containers. Planned work includes:

- Investigation of single and two-liquid phase responses to vibration
- Investigation of modulated 1g convective transport in solidifying succinonitrile-ethanol (SCN-E) and succinonitrile-water (SCN-W) melts using high and low frequency translational vibrations
- Comparison of thermosolutal and dominantly thermal convective responses to vibration (facilitated by the weak dependence of SCN-W density on composition)
- Investigation of the use of controlled vibration for transport control (e.g., for melt homogenization).

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THE EVOLUTION OF DENDRITE MORPHOLOGY DURING ISOTHERMAL COARSENING

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Abstract

Dendrite coarsening is a common phenomenon in casting processes. From the time dendrites are formed until the inter-dendritic liquid is completely solidified dendrites are changing shape driven by variations in interfacial curvature along the dendrite and resulting in a reduction of total interfacial area. During this process the typical lengthscale of the dendrite can change by orders of magnitude and the final microstructure is in large part determined by the coarsening parameters. Dendrite coarsening is thus crucial in setting the materials parameters of ingots and of great commercial interest.

This coarsening process is being studied in the Pb-Sn system with Sn-dendrites undergoing isothermal coarsening in a Pb-Sn liquid. Results are presented for samples of approximately 60% dendritic phase, which have been coarsened for different lengths of times. Presented are three-dimensional microstructures obtained by serial-sectioning and an analysis of these microstructures with regard to interface orientation and interfacial curvatures. These graphs reflect the evolution of not only the microstructure itself, but also of the underlying driving forces of the coarsening process. As a visualization of the link between the microstructure and the driving forces a three-dimensional microstructure with the interfaces colored according to the local interfacial mean curvature is shown.

Introduction

When a metal alloy is cast, solidification begins with the formation of a thin layer of solid metal at the surface of the mold. As the solidification front progresses into the ingot, however, the solidification front becomes unstable and forms dendrites throughout the remaining liquid. This partially solidified region is termed a mushy zone. The bulk of the ingot remains in the solid-liquid state for a substantial amount of time while heat is extracted and the interdendritic liquid solidifies. During this time the dendrites undergo a coarsening process that determines their ultimate morphology and length scale. The dendrite morphology and lengthscale in turn is crucial in setting the mechanical properties of the final ingot.

Research on dendrite coarsening was, until recently, restricted to examining either individual dendrites in transparent systems, see e.g. [1], or planar sections through a dendritic structure in opaque systems. Thus, the analysis of the evolution of the microstructure in opaque systems is usually reduced to determining the secondary dendrite arm spacing, λ_2 , as a function of coarsening time, see e.g. [2,3]. Such experiments show that $\lambda_2 \sim t_f^{1/3}$, where t_f is the time over which the solid and liquid coexisted. It is well known that dendrite coarsening is driven by the variation in mean interfacial curvature, H , along the interface between the solid (dendritic) and liquid (matrix) phase. This variation in curvature with position results in variations in the concentration of solute in the liquid along the interface as described by the Gibbs-Thomson equation,

$$x_A = x_A^0 + \ell_A^a H,$$

Keywords: dendrite coarsening, serial sectioning, interfacial curvature, characterization

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where x_A and x_A^0 are the concentration of A atoms at a curved and flat interface, respectively, ℓ_A^α is the capillary length in the α -phase and H is the mean curvature.

The variation in concentration with position along the dendrite interface in turn leads to diffusional fluxes between areas of high interface mean curvature, where solid dissolves, and areas of low interface mean curvature, where the solid grows. The overall effect is that the structure becomes coarser.

Several models have been proposed [4,5,6] to explain certain phenomenological aspects of the coarsening process. In general these models employ an oversimplified dendritic morphology and are limited to considering the evolution of localized areas of the dendrites. To formulate more realistic models, information on the complete topology of the dendritic structure and its evolution is required. This is because the solute flux, as discussed below, extends to large length scales. An overview on the coarsening of mushy zones and a discussion of the influence of the local interfacial shape on the coarsening process can be found in [10].

It is now possible to analyze the three-dimensional microstructure of ingots due to the development of a fully automated technique for serial-sectioning of metallic microstructures, which is capable of making 20-30 sections per hour, combined with a method to reconstruct three-dimensional microstructures using these sections [7]. This approach not only characterizes the morphology of the microstructure, but also allows the quantity that drives the coarsening process to be measured: the interfacial curvature as a function of position. For the first time microstructural evolution in dendritic mushes can be linked to its driving forces. The results can thus serve as a test of three-dimensional calculations of dendrite coarsening as well as provide much needed insight into the morphological evolution of topologically complex dendrites during coarsening.

Experimental Procedure

Ingots of Pb-80wt.%Sn have been directionally solidified in a Bridgman-like furnace to give a uniform dendritic microstructure containing ca 60% of Sn-dendrites and 40% of Pb-Sn eutectic phase. Cylindrical samples (6mm length, 12mm diameter) were cut from the rods using a wire cutter in order to preserve the microstructure. The samples were then coarsened at 185°C (2K above the eutectic temperature) for various lengths of time and subsequently quenched and serial-sectioned with a sectioning distance of 4.75 μ m. The microstructure was then reconstructed in a computer to give three-dimensional images and to conduct curvature analysis of the microstructure.

Analysis

Figure 1 shows the reconstructed volume for two samples that were held for 3 and 210 minutes at 185°C. Clearly, the dendritic microstructure coarsens over time. Figure 2 shows the inverse surface area per unit volume, a shape independent lengthscale measure, as a function of coarsening time.

Despite the large scatter of the data, a linear fit seems to agree reasonably well, which suggests that $\lambda_2 \sim t_f^{1/3}$. The interfacial curvature of the dendritic microstructure, shown in figure 1, was then determined. A full characterization of the curvature at each point of the interface requires either the mean and the Gaussian curvature, H and K , or equivalently the two principal curvatures, κ_1 and κ_2 , to be determined. Using mean and Gaussian curvature to characterize the structure is useful since the mean curvature, through the Gibbs-Thomson equation, sets the interfacial composition, and hence the dynamics of the coarsening process. Furthermore, the evolution of mean curvature is a function of the Gaussian curvature and vice versa, see [8]. Characterizing the local interface using the principal curvatures is, however, more intuitive. Figure 3

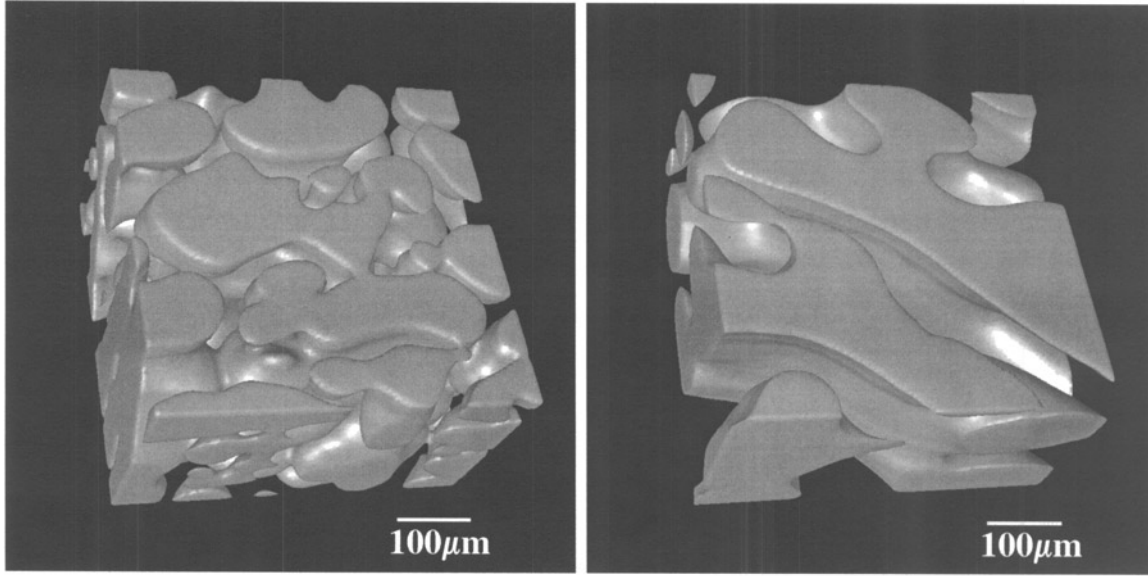


Figure 1. Reconstruction of the microstructure of Pb-80wt.%Sn samples coarsened for (a) 3 minutes and (b) 210 minutes at 185°C. The volume fraction of the dendritic phase, shown as solid, is approximately 60%. The matrix phase is not shown.

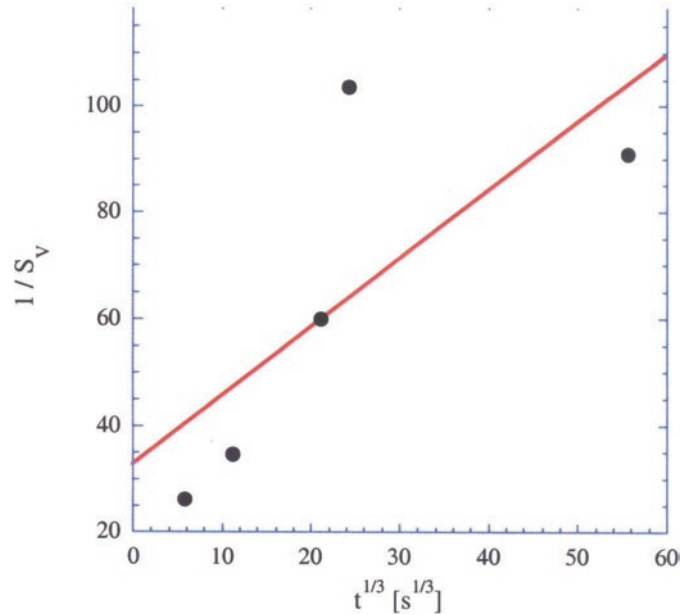


Figure 2. $1/S_v$ as a function of the cube root of the coarsening time.

shows the solid-liquid interfaces of the 3 minute sample colored based on the mean curvature (here a larger section of the microstructure is shown). Although the details of the microstructure are almost too small to be distinguished, one can clearly see that the sample contains regions of mostly negative mean curvature (bluish colors) and regions of mostly positive mean curvature (green/red colors). At this early stage the microstructure is clearly divided into these two kinds of regions. With ongoing coarsening, however, this separation diminishes.

Figure 5 (a) and (b) show the mean and Gaussian curvature as a probability density distribution for the 3 minutes and 2900 minutes coarsened samples. A map of the different regions and the according shapes can

be found in figure 4. In both cases we find a maximum at near spherical shapes and a distribution which declines from there. The total range of the distribution shrinks as the total lengthscale extends as one would expect from general coarsening theory. The coarsening is, however, not self similar. Using a similar representation in κ/κ_s - space this becomes more obvious (see figure 7, figure 6 for a map).

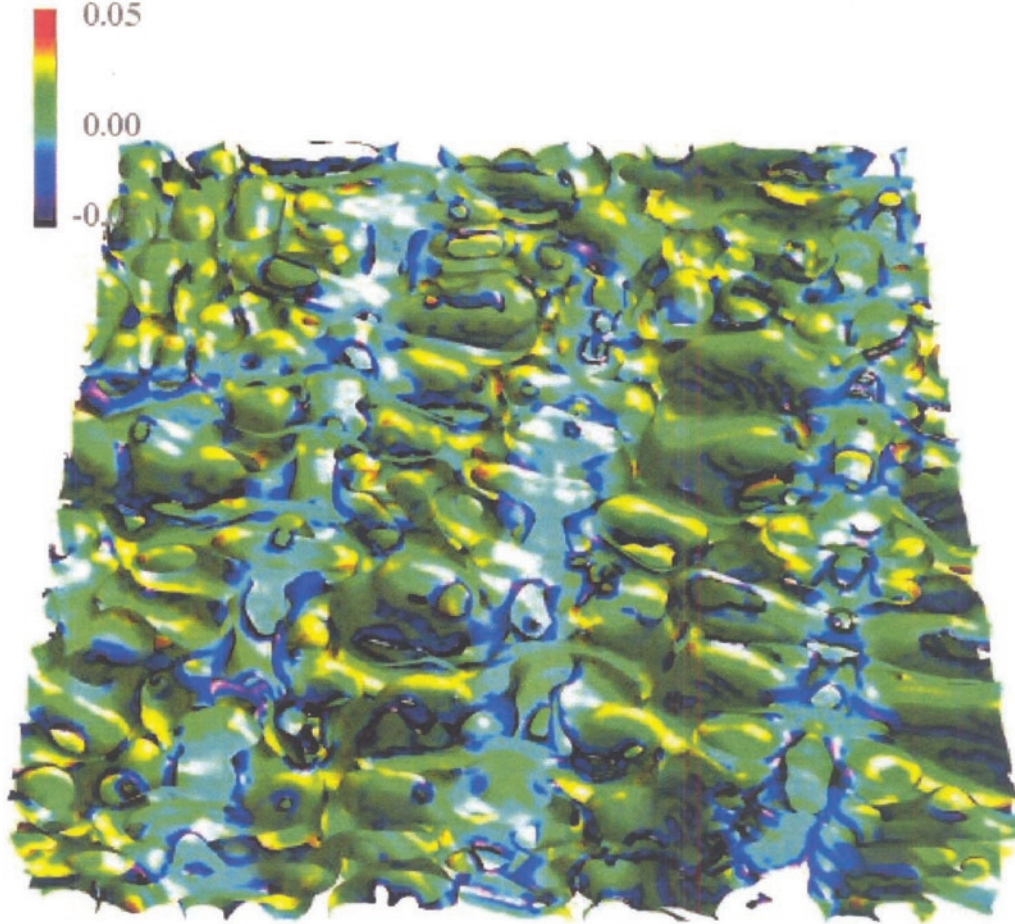


Figure 3. The interface of the 3 minute coarsened sample are shown colored based on the local mean curvature. The legend is given in the upper left corner.

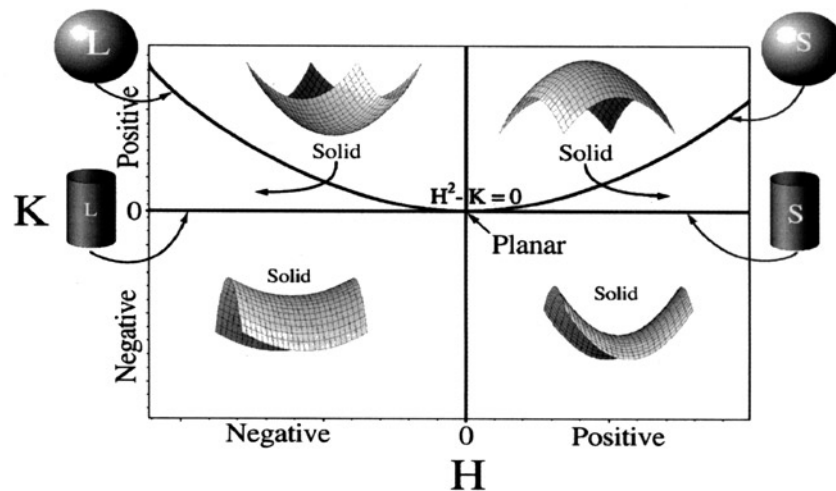


Figure 4. Map of the local interface shapes in the H - K space.

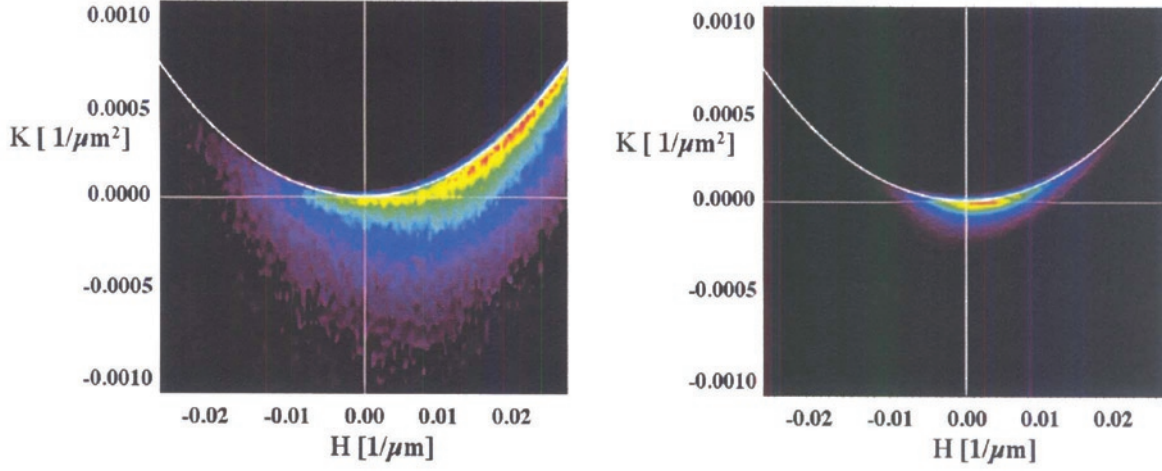


Figure 5: (a) and (b) show the probability density distributions in H - K - coordinates for the microstructures of the 3 minutes and 2900 minutes coarsened samples, respectively. The probability density function $P(H,K)$ is defined so that $P(H,K)dHdK$ is the probability that a randomly chosen interface point has a mean curvature between H and $H+dH$ and a Gaussian curvature between K and $K+dK$. The colors follow the rainbow with white/red as the highest probability density and black the lowest.

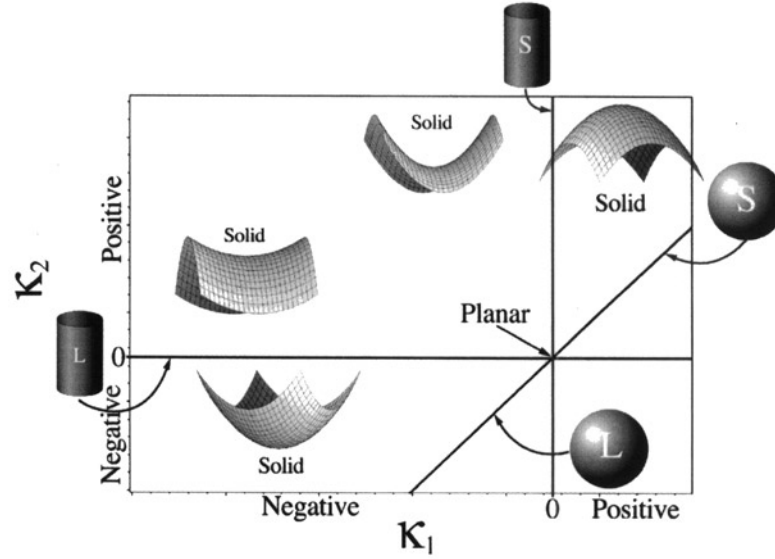


Figure 6: Map of the local interface shapes in the κ_1 / κ_2 -space.

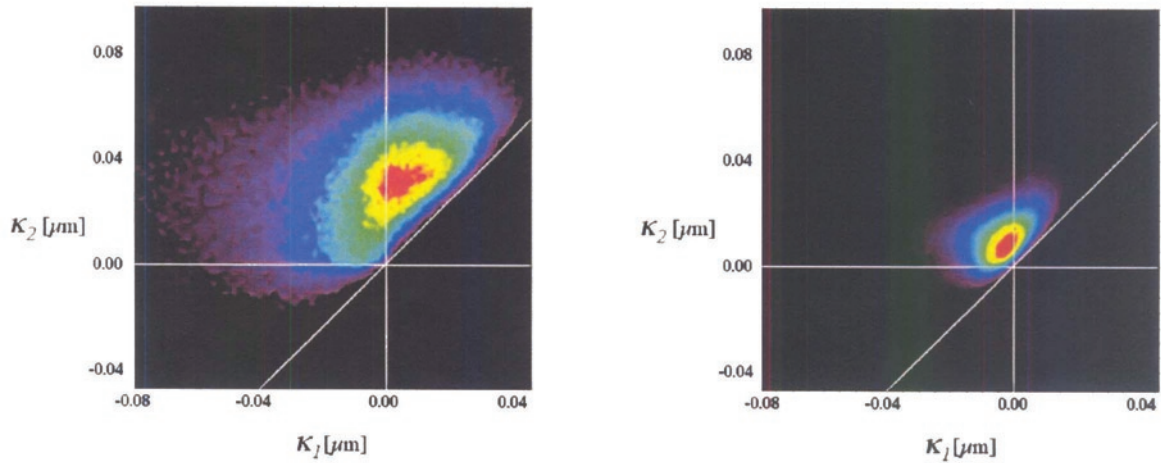


Figure 7: (a) and (b) show the probability density distributions in κ_1/κ_2 - coordinates for the microstructures of the 3 minutes and 2900 minutes coarsened samples, respectively. The probability density function is defined similar to the one used in figure 5.

The maximum for the 3 minute sample lies at positive κ_1 and κ_2 . If self similar coarsening were present this maximum would with increasing coarsening time drift towards 0/0. The 2900 minute coarsened sample shows, in contrast, that the maximum has actually moved across the $\kappa_1=0$ line.

Conclusions

The evolution of dendritic microstructures during isothermal coarsening for Pb-80wt.%Sn was studied. Using an automated serial-sectioning technique we obtained three-dimensional reconstructions of the dendritic microstructures coarsened for different lengths of time. These reconstructions can also be used to determine plots of the probability density of the mean and Gaussian curvatures. These plots show quantitatively the increase in size scale of a solid-liquid mixture that is expected during coarsening. Although the overall change in lengthscale suggests classic self-similar coarsening, plots of the curvature distributions show that the microstructure is undergoing morphological changes as it coarsens. This might eventually lead to a break up of the dendritic structure for very long coarsening times.

Information on the three-dimensional morphology will advance substantially our understanding of the dendrite coarsening process and will provide insights into the coarsening process that can be used to improve theoretical descriptions and simulations of the entire solidification process.

Acknowledgements

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FLOW VISUALIZATION OF LOW PRANDTL NUMBER FLUIDS USING ELECTROCHEMICAL MEASUREMENTS

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It is well established that residual flows exist in contained liquid metal processes. In 1-g processing, buoyancy forces often drive these flows and their magnitudes can be substantial. It is also known that residual flows can exist during microgravity processing, and although greatly reduced in magnitude, they can influence the properties of the processed materials. Unfortunately, there are very few techniques to visualize flows in opaque, high temperature liquid metals, and those available are not easily adapted to flight investigation.

In this study, a novel technique is developed that uses liquid tin as the model fluid and solid-state electrochemical cells constructed from Yttria-Stabilized Zirconia (YSZ) to establish and measure dissolved oxygen boundary conditions. The melt serves as a common electrode for each of the electrochemical cells in this design, while independent reference electrodes are maintained at the outside surfaces of the electrolyte. By constructing isolated electrochemical cells at various locations along the container walls, oxygen is introduced or extracted by imposing a known electrical potential or passing a given current between the melt and the reference electrode. This programmed titration then establishes a known oxygen concentration boundary condition at the selected electrolyte-melt interface. Using the other cells, the concentration of oxygen at the electrolyte-melt interface is also monitored by measuring the open-circuit potentials developed between the melt and reference electrodes. Thus the electrochemical cells serve to both establish boundary conditions for the passive tracer and sense its path.

Rayleigh-Bénard convection was used to validate the electrochemical approach to flow visualization. Thus, a numerical characterization of the second critical Rayleigh numbers in liquid tin was conducted for a variety of Cartesian aspect ratios. The extremely low Prandtl number of tin represents the lowest value studied numerically. Additionally, flow field oscillations are visualized and the effect of tilt on convecting systems is quantified.

Experimental studies of the effect of convection in liquid tin are presented. Three geometries are studied: (1) double electrochemical cell with vertical concentration gradients; (2) double cell with horizontal concentration gradients; and (3) multiple cells with vertical temperature gradients. The first critical Rayleigh number transition is detected with geometry (1) and it is concluded that current measurements are not as affected by convection as EMF measurements. The system is compared with numerical simulations in geometry (2), and oscillating convection is detected with geometry (3).

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Keywords: solid electrolytes, flow visualization, convection

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COUPLED GROWTH IN HYPERMONOTECTICS

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Introduction

The overall objective of this project is to obtain a fundamental understanding of the physics controlling solidification processes in immiscible alloy systems. The investigation involves both experimentation and the development of a model describing solidification in monotectic systems. The experimental segment was designed to first demonstrate that it is possible to obtain interface stability and steady state coupled growth in hypermonotectic alloys through microgravity processing. Microgravity results obtained to date have verified this possibility (1). Future flights will permit experimental determination of the limits of interface stability and the influence of alloy composition and growth rate on microstructure. The objectives of the modeling segment of the investigation include prediction of the limits of interface stability, modeling of convective flow due to residual acceleration, and the influence of surface tension driven flows at the solidification interface (2).

The study of solidification processes in immiscible alloy systems is hindered by the inherent convective flow that occurs on Earth and by the possibility of sedimentation of the higher density immiscible liquid phase. It has been shown that processing using a high thermal gradient and a low growth rate can lead to a stable macroscopically planar growth front even in hypermonotectic alloys (1,3). Processing under these growth conditions can avoid constitutional supercooling and prevent the formation of the minor immiscible liquid phase in advance of the solidification front. However, the solute depleted boundary layer that forms in advance of the solidification front is almost always less dense than the liquid away from the solidification front. As a result, convective instability is expected. Ground based testing has indicated that convection is a major problem in these alloy systems and leads to gross compositional variations along the sample and difficulties maintaining interface stability (4). Sustained low gravity processing conditions are necessary in order to minimize these problems and obtain solidification conditions that approach steady state.

The first phase of the Coupled Growth in Hypermonotectics (CGH) experiment flew aboard the Life and Microgravity Spacelab (LMS) mission during the summer of 1996. Processing conditions were controlled in an attempt to force the production of an aligned fibrous phase in the microstructure of processed samples. The Advanced Gradient Heating Facility (AGHF) was used to directionally solidify the immiscible alloys. Alloys in the aluminum-indium system were studied and specialized aluminum nitride ampoules were used in order to accommodate solidification shrinkage and to control thermal end effects (5). Three alloy compositions were processed during the LMS mission in order to permit comparison with the model over a composition range.

Keywords: immiscible alloys, hypermonotectics, monotectics, flight samples, directional solidification, flight

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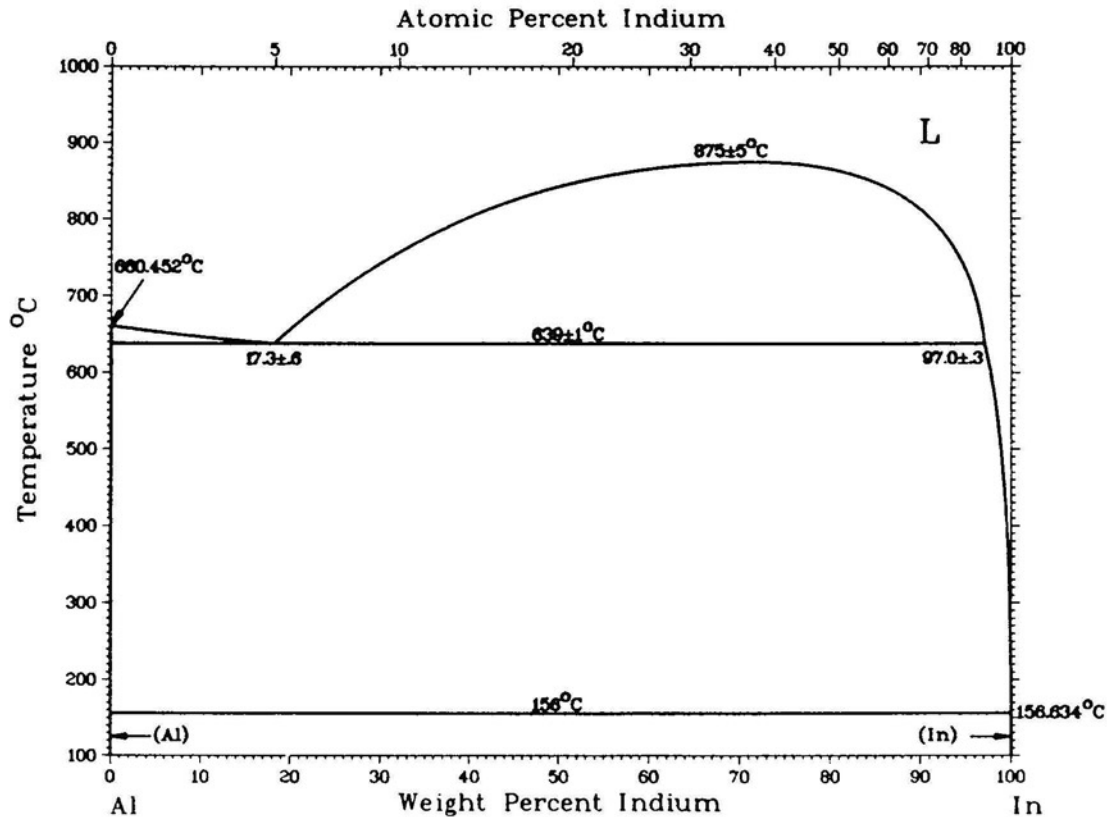


Figure 1. Phase diagram for the aluminum-indium alloy system (6).

Current efforts are concentrated toward both the preparation for upcoming experiments on the International Space Station and furthering the understanding of monotectics systems through ground based work. Two examples of projects in these areas are presented here.

Verification of Ampoule Material Stability

Aluminum nitride was used as the CGH ampoule material during the LMS mission. This material is now being considered for use by other investigators as well as for continued use for CGH experiments aboard the International Space Station. In an effort to further verify the suitability of aluminum nitride as an ampoule material, its stability under vacuum at elevated temperatures has been investigated. While meaningful data was gathered from the initial experiments conducted on the STS-78 LMS mission, some difficulties were encountered that warranted further investigation. It is imperative to determine if the difficulties encountered during the LMS mission were caused in part by the use of AlN ampoules under high temperature vacuum conditions.

Although great care was taken to prevent void formation during the LMS mission, post flight analysis revealed the presence of several small voids in the processed samples. Possible sources of the voids include a sticking piston, spring failure, seal failure, gas diffusion through the ampoule or seal, gas release due to decomposition or reaction of an ampoule component, and breakdown of the Al_2O_3 film usually present on any high aluminum content sample. Several of the above scenarios have been eliminated as void sources by extensive post-flight testing (6).

However, three of the previously mentioned possible mechanisms were not investigated in the above work. These mechanisms include the decomposition of aluminum nitride, its reaction with the contents of the ampoule, and the decomposition of the aluminum oxide film. LMS ampoules were hermetically sealed after loading under a vacuum of 1×10^{-4} mbar or better. During the CGH experiment, processing and sample homogenization temperatures of 1100°C were maintained for an extended period. Processing in high temperature vacuum conditions raises the concern of aluminum nitride dissociation. Possible reactions between the aluminum nitride ampoule and its various contents must also be considered as potential sources of gas formation. To help ensure the success of the CGH project, and to provide useful information to others who may use aluminum nitride as an ampoule material, its stability must be verified.

Testing Method

The testing conditions utilized (temperature and pressure) were chosen based on past processing conditions, as well as anticipated conditions for future experiments. In the LMS-CGH experiments, hot zone temperatures of 1100°C were used. In future experiments, temperatures up to 1200°C may be used in order to obtain the thermal gradients needed. In addition, local regions of the ampoule may see temperatures slightly higher than 1200°C due to the use of booster heaters. Thus, a temperature of 1250°C was selected to provide anticipated worst-case conditions in this study. The vacuum system used in this study is capable of maintaining vacuum levels of at least 1×10^{-7} mbar, making it ideal for the detection of gas evolution.

Samples were placed in a closed end high purity alumina tube for testing, which was inserted into a tube furnace (Figure 2). The alumina tube was connected to the vacuum chamber by an O-ring compression fitting. A residual gas analyzer was used to monitor for any possible gases released. A high-vacuum pump continuously evacuated the tube throughout the experiment. A vacuum level of 1×10^{-7} mbar or better was obtained during most of the testing run.

Three experimental conditions were tested: 1) as a control, the empty testing apparatus, 2) a section of aluminum nitride ampoule, and 3) the same section of aluminum nitride ampoule, but containing an aluminum-indium sample inside. In all three conditions, the system was pumped for eight hours at room

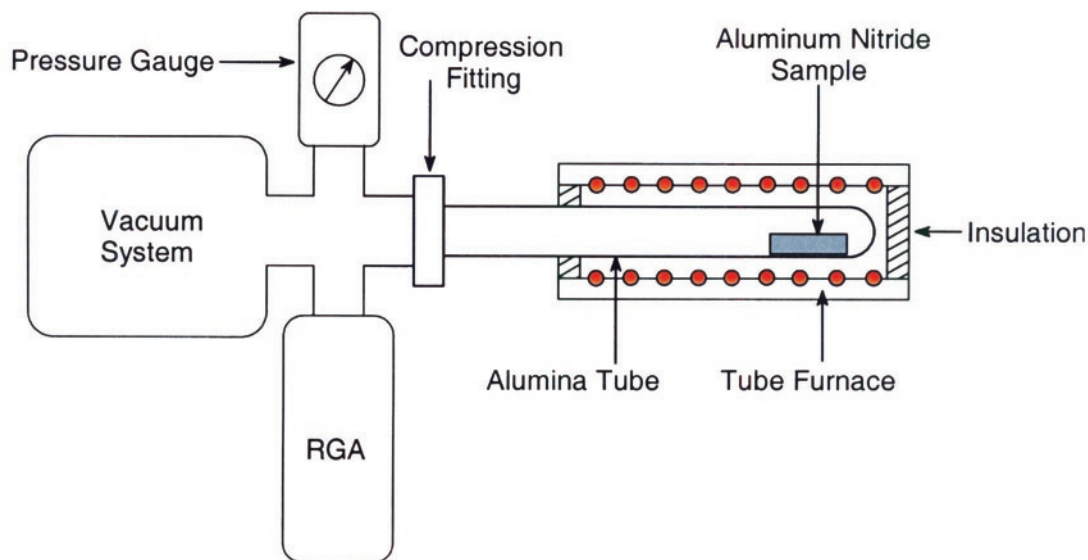


Figure 2. Schematic representation of experimental setup used to simulate processing conditions.

temperature prior to the beginning of the heating cycle. Vacuum levels of at least 1×10^{-7} mbar were achieved. Furnace temperatures were slowly increased to avoid thermal shock of the alumina tube. The final testing temperature was maintained at 1250°C for four hours. A residual gas analysis (RGA) system was used to collect spectra at regular intervals throughout the heating cycle and pressure levels were continuously monitored during the experiment. During each trial, mass units from 0-100 amu were monitored. This extended amu range was used so that unforeseen gases would not be missed by limiting the data collection to only a few select compounds.

Results and Conclusions

Analysis revealed that none of the spectra showed the presence of any unusual compounds. A spectra accumulated from a typical experimental run is shown in Figure 3. This figure illustrates the magnitudes of signal indications for the atomic mass unit range of 1-50 for each reading taken during the experiment. Thus, a specific species may be tracked with time. Inspection of the spectra from the three conditions revealed similar patterns, with the exception of nitrogen and oxygen levels. Comparisons between the three conditions were therefore performed on the basis of oxygen and nitrogen levels versus time.

The ampoule contents were considered when anticipating possible reactions. These contents include aluminum nitride, sintering aids, aluminum, the aluminum oxide film on the surface of the sample, indium, and any possible dissolved gases. Anticipated possible reactions include: the dissociation of aluminum nitride (to produce Al and N_2 gas), the breakdown of the aluminum oxide film (to produce Al and O_2 gas), and the reaction of the aluminum oxide film with molten aluminum (to produce O_2 and Al_2O gas). Data analysis led to the conclusion that these reactions do not occur to a sufficient degree for detection.

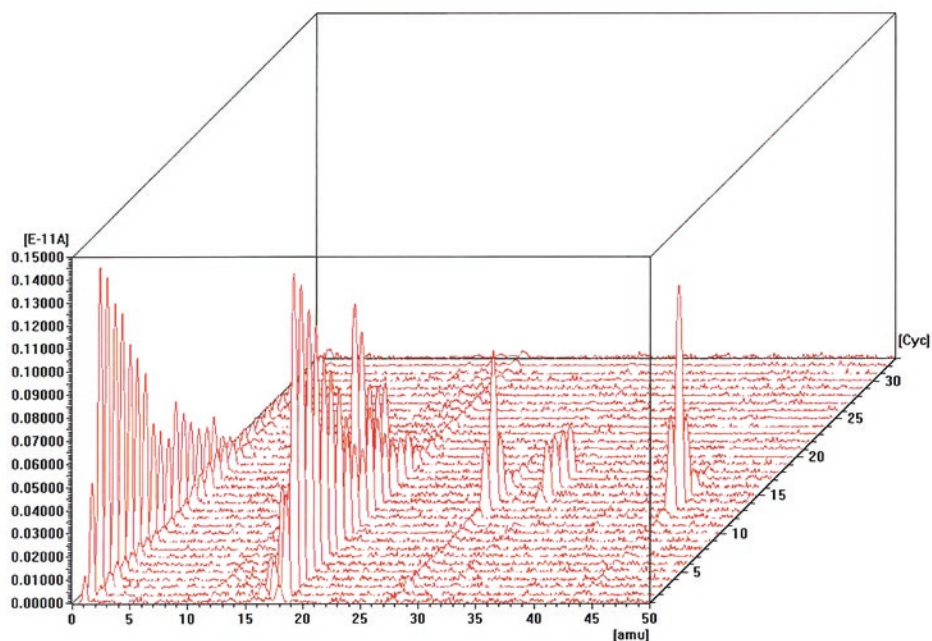


Figure 3. Typical RGA spectra obtained from an experimental run. Note that the signal amplitude for each atomic species, from 1-50 amu, is displayed versus measurement number. Thus, a species may be tracked with time.

This investigation resulted in three findings:

- 1) The aluminum nitride material used in this study does not significantly dissociate at temperatures of 1250°C and vacuum levels of 1×10^{-7} mbar.
- 2) An aluminum-indium alloy in contact with the aluminum nitride material investigated in this study does not result in a reaction that leads to measurable gas release under the testing conditions used.
- 3) The decomposition of Al_2O_3 to produce Al_2O was not detected under the testing conditions utilized.

Future Work

The testing apparatus is currently being modified to further improve sensitivity and obtain additional data. The modified assembly will permit determination of equilibrium vapor pressures at temperature in addition to the collection of gases over a long period of time. The collected gas can then be analyzed using the residual gas analysis system.

Alteration of Sample Thermal History During Processing

A composite-like microstructure should be attainable through directional solidification of alloys in monotectic systems if proper conditions are met during processing. Moving the composition “off-monotectic” can control the relative amounts of the phases in the composite, and in light of possible applications, the desired composition shift would be towards hypermonotectic.

Mollard and Flemings (7) found that, in order for fully fibrous composite-like growth to occur during solidification of off-eutectics, a minimum thermal gradient to growth velocity ratio (G/R) had to be maintained, in conjunction with suppressed convection. Due to the fact that monotectic systems are eutectic-type systems, a similar situation is anticipated in monotectics. Cahn (8) stated that, in addition to the Mollard and Flemings criteria, a monotectic system must possess a high miscibility gap for composite growth to be achieved during processing. Unfortunately, even for alloys of monotectic composition, it is common for the minor phase to assume a discontinuous morphology consisting of aligned spherical particles instead of a fibrous structure.

Numerous investigators have obtained microstructures that range from fully fibrous to fully spherical for alloys of monotectic composition. However, there exists some disagreement about the root cause of this morphology change in cases where both morphologies are present. One theory is that rods form and later breakdown via a Rayleigh type instability (9,10). Experimental evidence has also shown spheres forming at the solidification front in transparent metal analog systems (11).

The purpose of the current research is to study the effects of varying the time that a solidified sample spends at elevated temperature on the resulting microstructure by altering the rate of heat extraction from the sample. Enhanced heat extraction will reduce the time the just solidified section of the sample remains at elevated temperature and reduce the risk of fiber breakdown into rows of droplets. The primary approach is the attainment of efficient heat extraction by modifying the cold zone in a pre-existing Bridgman furnace so that conduction is the primary heat extraction mode.

Apparatus and Procedure

The cold zone of a standard 3-zone Bridgman furnace was redesigned such that several interchangeable configurations could be evaluated. The normal configuration consisted of a copper chill block where heat withdrawal occurred by convection between the crucible and chill block. A current modification of this configuration includes the addition of a conductive layer between the chill block and crucible to facilitate an increased rate of heat removal from the crucible. The conductive layer, VelTherm, is a velvet-like material consisting of carbon fibers, approximately 7 μm in diameter, oriented perpendicular to a polymeric backing sheet.

High purity (99.999) aluminum samples have been utilized to measure the thermal characteristics of the modified cold zone. Aluminum was used due to the fact that the thermophysical properties are well known. The data obtained will provide a general idea of the effectiveness of the modifications. Eventually, aluminum-indium alloys will be utilized for measuring the thermal characteristics and evaluating microstructural changes.

Procedures

Two experimental conditions were evaluated in this study. The first condition utilized a rounded bottom alumina crucible and a 9.5mm bore cold zone insert that closely mimicked the unmodified furnace configuration. The second condition utilized a modified crucible that was essentially an alumina tube plugged with thermal cement at one end combined with a cold zone insert containing a VelTherm layer. In this case a 1.5 mm thick VelTherm layer was in contact with the modified crucible. The VelTherm product used has a thermal conductivity value of 100 W/m-K, and was attached directly to the internal bore of the cold zone insert with epoxy film. Thus a continuous heat conduction path was established from the outer crucible wall to the cold zone insert.

The temperature of the hot zone was maintained at 1100 $^{\circ}\text{C}$, and the cold zone temperature was held at 30 $^{\circ}\text{C}$. A furnace translation rate of 6 $\mu\text{m/s}$ was utilized.

Results

Temperatures at the bottom of the aluminum samples were monitored during processing and are presented in Figure 4. The blue curve in the figure corresponds to the standard configuration, while the red curve corresponds to the modified configuration. A comparison of these curves reveals that if a sample is solidified under standard processing conditions, the alloy near the bottom of the sample will remain between the monotectic temperature (639 $^{\circ}\text{C}$) and the eutectic temperature (156 $^{\circ}\text{C}$) of the aluminum-indium system for a time period greater than 13,000 seconds. However, if a sample is solidified under the modified set of conditions, the alloy near the bottom of the crucible will remain between the monotectic and eutectic temperatures of the aluminum-indium system for a time period of approximately 4,300 seconds. The use of the modified configuration results in a dramatic reduction in the “time at temperature” to one-third of the time for the standard configuration. The time available for rod breakdown is reduced by approximately 8,700 seconds. These results obviously indicate that the modified crucible configuration and carbon fiber heat transfer path drastically enhance the heat extraction rate. It is hoped that this increased cooling rate will have a positive impact on the ability to maintain a fibrous microstructure in directionally solidified monotectic alloys. Future work using monotectic alloys will evaluate the influence of this modification on resulting microstructures.

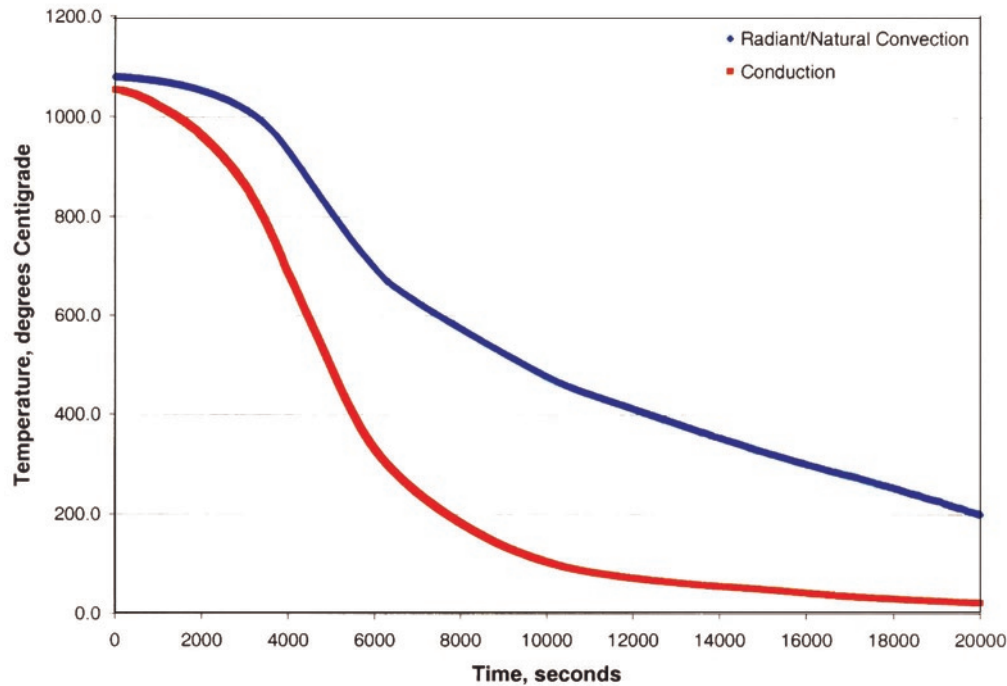


Figure 4. Thermal history plot for the two cold zone / crucible configurations

Future Work

The next step in this investigation involves solidifying alloys of monotectic composition and performing metallographic investigations to determine the effects of efficient heat extraction on the microstructure. Depending on the results of these investigations, the heat extraction rate may be enhanced further by the construction of a cold zone insert that utilizes a low melting point metal heat conduction path.

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CONVECTIVE EFFECTS DURING DIFFUSIVITY MEASUREMENTS IN LIQUIDS WITH AN APPLIED MAGNETIC FIELD

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Abstract

Convective contamination of self-diffusion experiments with an applied magnetic field is considered using a two-dimensional axisymmetric model. Constant, uniform, and an additional non-uniform heat fluxes are imposed along the sidewall of the cylinder while constant heat loss occurs through the top and bottom. In this model, due to a very small thermal Peclet number, convective heat transfer is neglected, and the flow is steady and inertialess. Time-dependent concentration is solved for various values of the mass Peclet number, Pe_m , (the ratio between the convective transport rate and the diffusive transport rate) and different magnetic field strengths represented by the Hartmann number Ha . Normalized values of these diffusivities vs. effective Pe_m are presented for different imposed temperature profiles. In all cases, the diffusivity value obtained through the simulated measurement increases as the effective Pe_m increases. The numerical results suggest that an additional periodic flux, or “hot” and “cold” spots, can significantly decrease the convective contamination in our geometry.

1. Introduction

During liquid self-diffusion experiments, a small non-uniformity in temperature within the melt may drive buoyant convection. This convection can result in erroneous values of the measured diffusivity. Verhoeven [1] emphasized that any horizontal component of a density gradient in the liquid results in spontaneous convection with no threshold. Alexander et al. [2] showed that for three-dimensional (3D) time-dependent transport in the presence of gravity with horizontal temperature non-uniformities across the sample as low as 1 and 0.1 K, convective transport rates in 1 and 3 mm capillaries, respectively, can exceed diffusive transport rates, and, thus, result in higher values of measured diffusivities. Alexander and Banish [3] presented the results of combined numerical modeling and order-of-magnitude estimates of the sensitivity of convective contamination to low-gravity in self-diffusion experiments.

Applied magnetic fields have been used to suppress the buoyant convection in the liquid metals and semiconductors due to their large electrical conductivities [4-6]. Youdelis et al. [7] showed that at high magnetic field strengths, the diffusion process itself can be significantly modified through the Lorentz body force acting on the conducting liquids ions and electrons. Alboussiere et al. [8] found that with electromagnetic damping the convective contribution to the effective mass Peclet number is scaled as Hartmann number Ha^4 .

Keywords: self-diffusivity, convection, magnetic fields, thermal asymmetries, flight

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In actual self-diffusivity experiments, measured diffusivity results that deviate by less than 5% from the (known) real value, D_0 , would be considered “acceptable. The purpose of this paper is to quantitatively estimate the magnitude of allowable temperature non-uniformities in the liquid that will guarantee that measured diffusivity values lie within 5% of the actual value when the experimental system is subject to an axial magnetic field. To model the experiment, axisymmetric, time-dependent transport due to a combination of steady flow and diffusion is considered. In this basic model, a steady, uniform heat flux that produces a radial temperature difference in the liquid is imposed on the sidewall of the cylindrical container while uniform heat losses are imposed on the top and bottom walls. Then, a steady, spatially-periodic heat flux is superimposed on the sidewall of the cylinder to predict the effect of spatial temperature variations which represent the localized hot and cold spots along the sidewall. Note that the overall flux for this additional periodic condition is zero. Simulated diffusivity results for two different magnetic field strengths and five various temperature profiles along the sidewall are presented in this paper.

2. Problem Formulation

In this model, a Boussinesq fluid contained in a closed vertical circular cylinder of length $Z = 30$ mm with an inside radius R of 1.5 mm. Gravity acts downward along the cylinder axis while a uniform axial magnetic field is applied in the opposite direction as in Fig. 1a. The origin lies at ($R = 0$) and $z = Z/(2R)$. The isopicnic radioactive tracer is initially located at the bottom of the cylinder. The dimensionless model has the top and bottom limits of $z = 10$ and -10 , respectively, while the vertical wall lies at $r = 1$.

2.1. Thermal Problem

For sufficiently large values of magnetic field strength B , the magnetic damping results in a characteristic ratio of convective to conductive heat transfer (the thermal Péclet number, $Pe = \rho c_h UR/\lambda$, where ρ is uniform density, c_h is the specific heat, U is a characteristic velocity and λ is the thermal conductivity) is small; the dimensionless temperature in this case is then governed by $\nabla^2 T = 0$. Therefore, in this model, we assume that convective heat transfer is negligible (i.e., $Pe \ll 1$) and that a uniform heat flux density is imposed along the vertical wall and constant heat losses through the top and bottom walls of the cylinder with the possibility of an additional spatially-periodic heat flux of various amplitude and wavelength on the vertical sidewall in some cases. With these assumptions, the energy equation ($\nabla^2 T = 0$) is non-dimensionalized by R for length and $2\Delta T_r$ for temperature, where ΔT_r is the temperature difference between the centerline and the vertical (side) wall and the dimensionless analytical solution for temperature is

$$T(r, z) = s_1 \left(\frac{r^2}{2} - z^2 \right) + s_2 I_0(ar) \cos(az), \quad (1)$$

where $a = n\pi/10$ and n is a known integer, s_1 and s_2 are set coefficients, and I_0 is a modified Bessel function of the first kind of order zero. The first term on the right hand side of Eq. (1) represents the temperature distribution due to a uniform heat flux while the second term represents the temperature distribution due to a spatially-periodic heat flux.

2.2. Flow Problem

At sufficiently large values of B , the characteristic ratio of the electromagnetic body force to the inertial effect (the interaction parameter, $N = \sigma B^2 R / (\rho U)$, where σ is the electrical conductivity of the liquid) is very large and, thus, the inertial terms in the Navier-Stokes equations become negligible. In addition to the applied magnetic field produced by the magnet, associated electric currents induce an additional magnetic field since the materials considered here are electrically conducting. The characteristic ratio of

the induced to applied magnetic field strengths is the magnetic Reynolds number, $R_m = \mu_p \sigma UR$, (where μ_p is the magnetic permeability of the liquid) and this is very small for crystal growth processes and self-diffusion experiments of liquid metals and semiconductors. Thus, neglect of the induced magnetic field effect is justifiable in the model presented here.

Khine and Walker [9] determined the characteristic velocity for magnetically damped axisymmetric buoyant convection $U = 2\rho g_0 \beta \Delta T_r / (\sigma B^2)$, where g_0 is the gravitational acceleration (9.81 m/s^2) and β is the volumetric expansion coefficient for Boussinesq approximation, and this is used to non-dimensionalize the velocity. The magnetic flux, reduced pressure (the difference between the total pressure and the hydrostatic pressure) with uniform density, the electric current density, and the electric potential are non-dimensionalized using B , $\sigma UB^2 R$, σUB , and UBR , respectively. The dimensionless, inertialess equations governing the steady, axisymmetric buoyant convection are then

$$\nabla \cdot \mathbf{v} = 0, \quad (2a)$$

$$\nabla p = T \hat{z} + \mathbf{j} \times \hat{z} + Ha^2 \nabla^2 \mathbf{v}, \quad (2b)$$

$$\nabla \cdot \mathbf{j} = 0, \quad (2c)$$

$$\mathbf{j} = -\nabla \phi + \mathbf{v} \times \hat{z}. \quad (2d)$$

Here, $Ha = BR(\sigma/\mu)^{1/2}$, where μ is the viscosity of the liquid, Eq. (2a) is the conservation of mass, Eq. (2b) is the Navier-Stokes equation with a buoyancy force and an electromagnetic body force, Eq. (2c) is the continuity of electric current density $\mathbf{j}$, and Eq. (2d) is Ohm's law with an electric potential function ϕ . We eliminated the pressure p , by introducing a stream function, $\psi(r, z)$ which satisfies Eq. (2a).

The boundary conditions are

$$\psi = \frac{\partial \psi}{\partial r} = 0, \text{ at } r = 1; \quad (3a)$$

$$\psi = 0, \text{ at } z = -10, 10. \quad (3b)$$

We used the Chebyshev spectral collocation method to solve the equation governing $\psi(r, z)$.

2.3. Diffusion Problem

The dimensionless axisymmetric governing equation for diffusion is

$$\frac{\partial c}{\partial t} + Pe_m \mathbf{v} \cdot \nabla c = \nabla^2 c. \quad (4a)$$

Here, t is normalized by the diffusion time scale (R^2/D_0) and c is scaled by the initial concentration C_0 . $Pe_m = UR/D_0$ is the characteristic ratio of convective effects to diffusive effects in the process. Here, U is the calculated characteristic velocity and differs from case to case. Since there is no mass transfer across any boundary, the boundary conditions are

$$\frac{\partial c}{\partial r} = 0, \text{ at } r = 1; \quad (4b)$$

$$\frac{\partial c}{\partial z} = 0, \text{ at } z = -10, 10. \quad (4c)$$

Eq. (4a) is solved for different Pe_m with conditions (4b, 4c) using a Chebyshev spectral collocation method for spatial discretization as in the flow problem while conventional finite-difference is used for temporal discretization.

The initial condition for c where tracer forms a thin layer at the bottom of the cylinder is represented by

$$c(r, z, t=0) = \exp(-\alpha(z+10)^2), \quad (5)$$

where $\alpha = 3$ and dramatically to $c \approx 0$ around $z = -9$. The simulated measurements (or output diffusivities D) are computed from the resulting time traces of concentration through a straight line fit in the form,

$$\ln[c_1(t) - c_2(t)] = \text{constant} - \left(\frac{\pi^2 D}{Z^2} \right) t \quad (6)$$

which is known as Codastefano [11] or Harned [12] technique. c_1 and c_2 are concentration measured at $z = Z/6$ and $5Z/6$ along the length of the cylinder, respectively, and the *constant* depends on the concentration profile $c(z)$ at $t = 0$.

In the flow problem, 15 collocation points are needed in the radial direction and 40 points in the axial. In the diffusion problem, the total number of collocation points in r is 15 and that in z is 80 since the entire cylinder is considered. Liquid indium with $\beta = 1.02 \times 10^{-4} \text{ K}^{-1}$, $\rho = 6.64 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$ and $\sigma = 3.02 \times 10^6 \text{ S} \cdot \text{m}^{-1}$ [13] is used as a model fluid. A self-diffusivity value of $D_0 = 1.48 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ was used as the input. Two different Hartmann numbers are considered. For liquid indium these correspond to magnetic field strengths of 0.218 T ($Ha = 25$) and 0.873 T ($Ha = 100$). The characteristic diffusion time is 1520 s, and values of Pe_m between 0 and 4 are considered here.

3. Results and Discussion

The results for five different incoming heat fluxes (see Figs. 1b to 1f) are presented in this section. Case I presents self-diffusion with a radial temperature difference only as the driving force in the liquid due to the steady, uniform heat flux along the sidewall. Cases II through V present self-diffusion with various magnitude of uniform heat flux and superimposed, steady, spatially-periodic heat flux with various amplitude and wavelength along the sidewall (i.e., localized hot and cold spots along the sidewall in addition to the radial temperature difference in the liquid). The desired incoming heat fluxes for Cases I through V are obtained by adjusting s_1 , s_2 and a in Eq. (1). Table I presents summarized results for those five different cases.

Case I: $s_1 = 1$ and $s_2 = 0$ in Eq. (1)

In this case, a uniform heat flux of density 1 that produces a radial temperature difference in the liquid is applied through the vertical wall with uniform heat loss through the top and bottom end walls as in Fig. 1b. The isotherms show symmetry from $z = 0$ plane, and are slightly deviated from the horizontal, and decrease toward the top and bottom walls. The streamlines for both Ha circulate in counterclockwise motion beginning near the vertical wall.

Figure 2 presents the diffusivity vs. effective Pe_m for $Ha = 25$ and 100. For both Ha , the results lie on one curve that bows upward as the effective Pe_m increases. From the results, we can see that the convective effect is extremely large for a larger effective Pe_m . For effective $Pe_m < 2$, the predicted convective effect in self-diffusivity measurements (i.e., difference in diffusivity from D_0) is less than 5% for both $Ha = 25$ and 100. The allowable driving force ΔT_r for $Ha = 25$ is about 0.00373 K while that for $Ha = 100$ is about 0.00501 K to prevent convective contamination in excess of 5%.

Case II: $s_1 = s_2 = 1$ and $n = 3$ in Eq. (1)

In this case, the uniform heat flux is the same as in Case I which produces a radial temperature difference in the liquid while a periodic flux with an amplitude of 0.495 is superimposed at the sidewall to produce the localized periodic temperature variation effect. Here, $n = 3$ represents the number of periodicity in the non-uniform heat flux. The maxima of the periodic flux occur at $z = -6.67, 0$ (mid-plane), and 6.67 while the minima occur at $z = -10$ (bottom wall), $-3.33, 3.33$, and 10 (top wall). So, the top and bottom walls, $z = Z/6$ and $5Z/6$ are slightly cooler than the rest of the cylinder.

For Case II, the diffusivity results are plotted in Fig. 3 for both values of Ha . Again, the two curves bow upward as the effective Pe_m increases. The curve for $Ha = 100$ is slightly higher than that for $Ha = 25$. The difference is more obvious at a larger effective Pe_m . For the diffusivity results of less than 5% deviation from D_0 , the allowable ΔT_r for $Ha = 25$ is 0.00373 K and that for $Ha = 100$ is 0.00548 K. Case II results are very close to those of Case I. The spatially-periodic temperature along the sidewall does not affect the diffusivities significantly although the presence is observed in the flow pattern.

Case III: $s_1 = 0.01, s_2 = 1$, and $n = 3$ in Eq. (1)

As shown in Fig. 1d, the uniform heat flux with a magnitude of 0.01 (i.e., 100 times smaller than that in Case I) and a spatially-periodic flux with an amplitude of 0.495 (same as in Case II) are imposed at the sidewall. For Case III, the consequences of the magnetic field for transport can be seen from the diffusivity vs. the effective Pe_m shown in Fig. 3. For both Ha , the curves bow upward as the effective Pe_m increases. The effect of convection on the measured diffusivity is more prominent at a larger effective Pe_m . Also, the diffusivity curve for $Ha = 100$ lies above the curve for $Ha = 25$. For less than 5% deviation from D_0 , the driving ΔT_r for $Ha = 25$ is about 0.0249 K while for $Ha = 100$, it is 0.171 K. Thus, Case III suggests that reducing the radial temperature gradient in the liquid by 100 times from its original value (as in Case I) has a tremendous effect on the diffusivity results for this model. The effect is more prominent at higher Ha for this case (i.e., at stronger magnetic field strength).

Case IV: $s_1 = 0.001, s_2 = 1$, and $n = 3$ in Eq. (1)

Here, the uniform heat flux which produces a radial temperature difference in the liquid is further reduced to a magnitude of 0.001 (i.e., 10 times less than that in Case III and 1000 times less than that in Case I) while keeping the periodic temperature profile unchanged as in Cases II and III. The diffusivity vs. effective Pe_m for Case IV is shown in Fig. 3 for both Ha . As in the previous case, the two curves bow upward as the effective Pe_m increases, and the curve for $Ha = 100$ is higher than that for $Ha = 25$, especially at larger effective Pe_m . The allowable ΔT_r in this case for $Ha = 25$ is 0.0262 K while that for $Ha = 100$ is 0.184 K which is a slight improvement from those in Case III. Thus, reducing the magnitude of radial temperature gradient by 10 times from Case III does not result in tremendous changes in diffusivity results.

Case V: $s_1 = 0.01, s_2 = 1$, and $n = 2$ in Eq. (1)

This case is the same as Case III except $n = 2$ here so that the isotherms decrease and increase two times alternatively in between the top and bottom walls (i.e., the periodicity is 2 here). The uniform flux which produces the radial temperature difference is 100 times smaller than that in Case I. The maxima of spatially-periodic flux occur at $z = -10$ (bottom wall), 0 (mid-plane), and 10 (top wall) with a magnitude of 0.207 while the minima occur at $z = -5$ and 5 . So, the top and bottom walls and the mid-plane are slightly warmer than the rest of the cylinder.

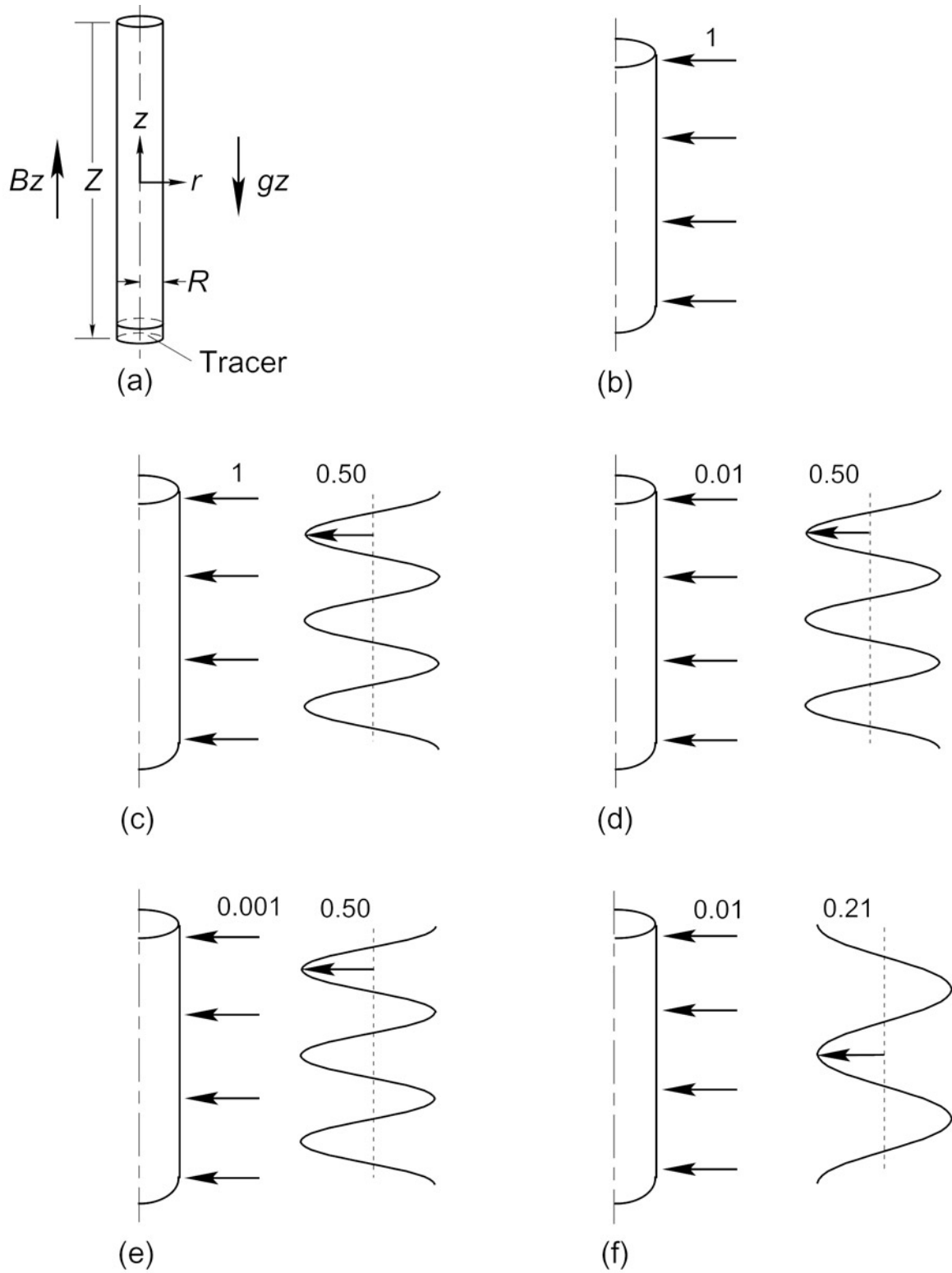


Fig. 1 Model diffusion capillary. Fig. 1a presents the set up and Figs. 1b - 1f describe the dimensionless incoming heat fluxes for Cases I through V.

The diffusivities vs. effective Pe_m for Case V are plotted in Fig. 3 for both Ha . The curve for $Ha = 100$ is higher than that for $Ha = 25$ and the convective effects are more obvious at larger effective Pe_m . In this case, the allowable temperature non-uniformity ΔT_r for $Ha = 25$ is 0.0426 K and that for $Ha = 100$ is 0.222 K . The results are close to those of Case III with an improvement in sensitivity of allowable temperature for the same magnetic field strength.

4. Conclusions

The use of an axial magnetic field to offset the detrimental effects of convection on diffusivity measurements in liquid metals has been examined using a numerical model. Our goal was to determine what magnetic field strengths would be necessary given various temperature non-uniformities to ensure that convective transport was less than 5% of the diffusive. Two different flow patterns were observed for the various imposed temperature non-uniformities. For a uniform heat flux along the sidewall that produces a radial temperature difference in the liquid, the streamlines form a counterclockwise motion. For a spatially-periodic heat flux which produces the localized hot and cold spots on the vertical wall, the flow is arranged as vertically stacked cells and the number of cells depends on the periodicity of the temperature profile due to periodic flux.

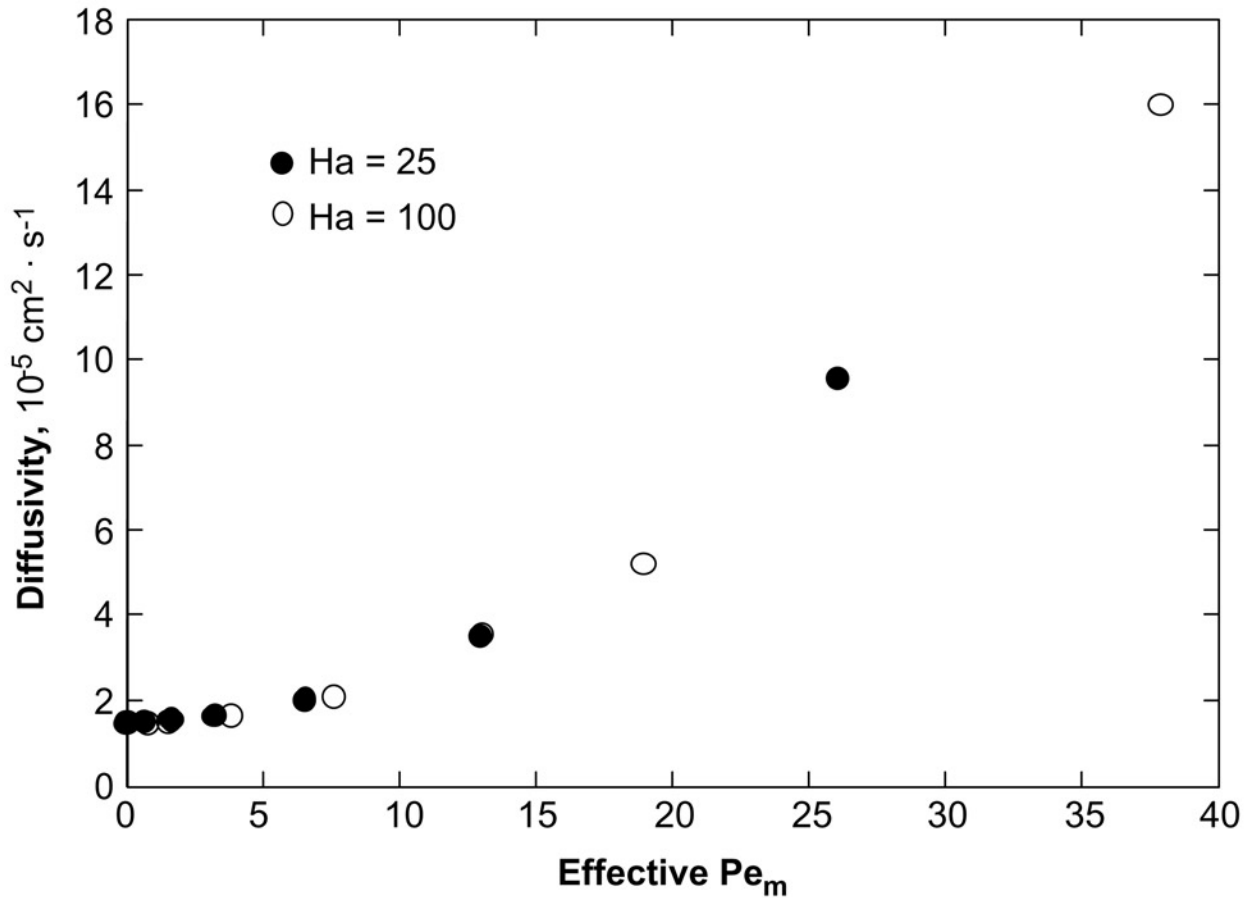


Fig. 2 Diffusivity vs. effective Pe_m for Case I.

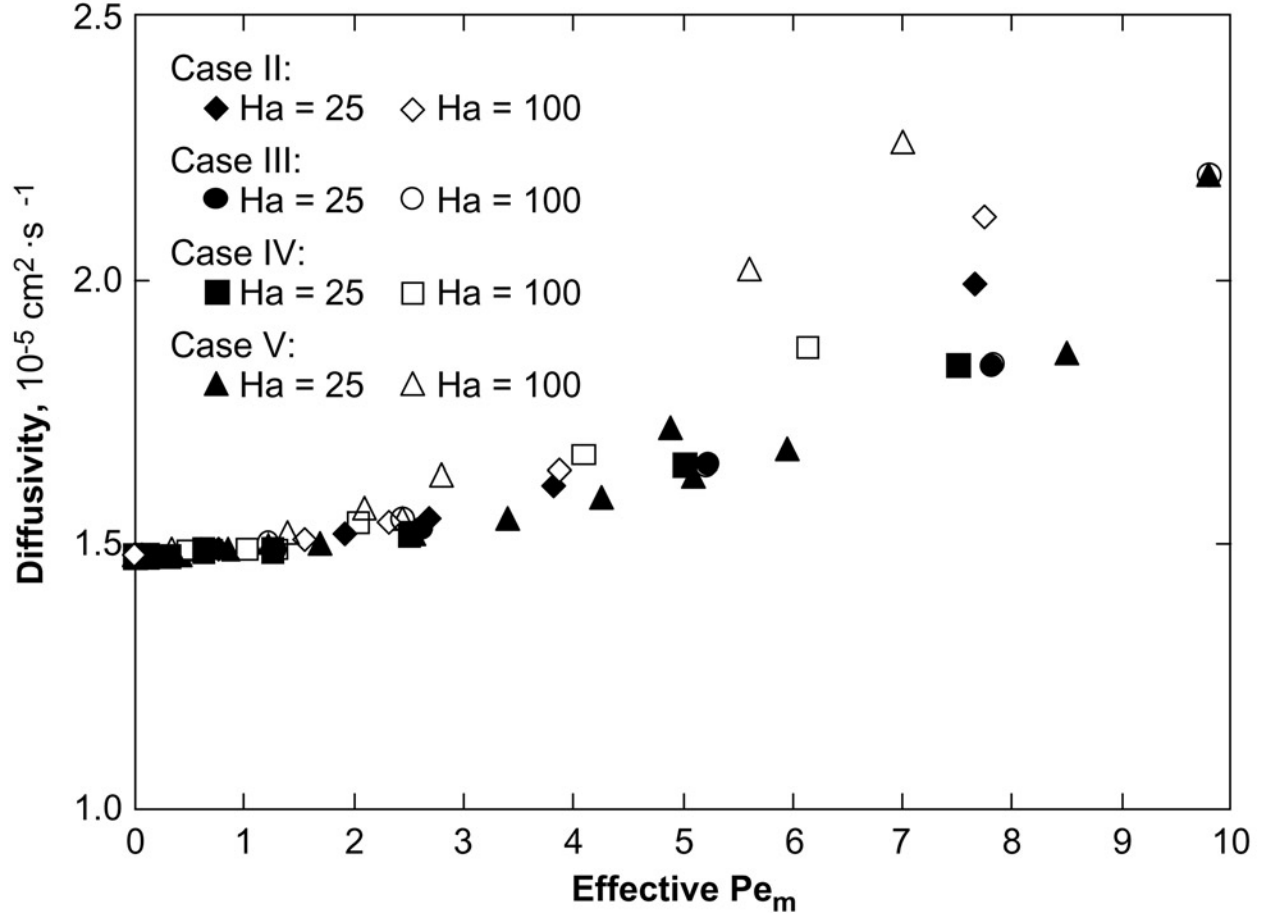


Fig. 3 Diffusivity vs. effective Pe_m for Cases II, III, IV and V.

Table 1. Summary of results for Cases I – V.
Case I: uniform heat flux only; $d=1$, $e=0$ in Eq. (1)

$B = 0.218T$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
$Ha = 25$	0.00107	7.34×10^{-6}	6.42×10^{-5}	9.87×10^{-6}	0.651	1.49
	0.00373	2.57×10^{-5}	2.25×10^{-4}	3.46×10^{-5}	2.28	1.55
	0.0107	7.34×10^{-5}	6.42×10^{-4}	9.87×10^{-5}	6.51	1.99
	0.0426	2.94×10^{-4}	2.57×10^{-3}	3.95×10^{-4}	26.04	9.57
$B = 0.873T$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
$Ha = 100$	0.00171	2.85×10^{-6}	7.48×10^{-5}	9.87×10^{-7}	0.758	1.49
	0.00501	8.35×10^{-6}	2.19×10^{-4}	2.89×10^{-6}	2.22	1.55
	0.0171	2.85×10^{-5}	7.48×10^{-4}	9.87×10^{-6}	7.58	2.11
	0.0854	1.43×10^{-4}	3.74×10^{-3}	4.93×10^{-5}	37.9	16.0

Case II: uniform flux $\sim$ periodic flux; $d = 0.01$, $e = 1$ and $n = 3$ in Eq. (1)

$B = 0.218T$ $Ha = 25$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.00533	8.78×10^{-6}	6.41×10^{-5}	4.93×10^{-5}	0.652	1.49
	0.0249	4.11×10^{-5}	3.00×10^{-4}	2.31×10^{-4}	3.04	1.55
	0.0639	1.05×10^{-4}	7.70×10^{-4}	5.92×10^{-4}	7.82	1.84
$B = 0.873T$ $Ha = 100$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.0427	8.46×10^{-6}	6.04×10^{-5}	2.47×10^{-5}	0.612	1.49
	0.171	3.38×10^{-5}	2.42×10^{-4}	9.87×10^{-5}	2.45	1.55
	0.684	1.35×10^{-4}	9.67×10^{-4}	3.95×10^{-4}	9.79	2.2

Case III: uniform flux ~ 100 * periodic flux; $d = e = 1$ and $n = 3$ in Eq. (1)

$B = 0.218T$ $Ha = 25$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.00107	5.92×10^{-6}	7.56×10^{-5}	9.87×10^{-6}	0.766	1.49
	0.00373	2.07×10^{-5}	2.65×10^{-4}	3.45×10^{-5}	2.68	1.55
	0.0107	5.92×10^{-5}	7.56×10^{-4}	9.87×10^{-5}	7.66	1.99
$B = 0.873T$ $Ha = 100$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.00171	2.83×10^{-6}	7.64×10^{-5}	9.87×10^{-7}	0.774	1.49
	0.00548	9.07×10^{-6}	2.45×10^{-4}	3.16×10^{-6}	2.48	1.55
	0.0171	2.83×10^{-5}	7.64×10^{-4}	9.87×10^{-6}	7.74	2.12

Case IV: 10 * uniform flux $\sim$ periodic flux; $d = 0.001$, $e = 1$ and $n = 3$ in Eq. (1)

$B = 0.218T$ $Ha = 25$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.00533	8.78×10^{-6}	6.17×10^{-5}	4.93×10^{-5}	0.624	1.49
	0.0262	4.31×10^{-5}	3.03×10^{-4}	2.42×10^{-4}	3.07	1.55
	0.0639	1.05×10^{-4}	7.40×10^{-4}	5.92×10^{-4}	7.50	1.84
$B = 0.873T$ $Ha = 100$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.0427	8.61×10^{-6}	5.06×10^{-5}	2.47×10^{-5}	0.513	1.49
	0.184	3.71×10^{-5}	2.18×10^{-4}	1.06×10^{-4}	2.21	1.55
	0.513	1.03×10^{-4}	6.07×10^{-4}	2.96×10^{-4}	6.15	1.87

Case V: uniform flux $\sim$ periodic flux; $d = 0.01$, $e = 1$ and $n = 2$ in Eq. (1)

$B = 0.218T$ $Ha = 25$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.0107	1.04×10^{-5}	8.39×10^{-5}	9.87×10^{-5}	0.850	1.49
	0.0426	4.14×10^{-5}	3.35×10^{-4}	3.95×10^{-4}	3.40	1.55
	0.107	1.04×10^{-4}	8.39×10^{-4}	9.87×10^{-4}	8.50	1.86
$B = 0.873T$ $Ha = 100$	ΔT_r (K)	$ v_{r \max} $ (cm/s)	$ v_{z \max} $ (cm/s)	U (cm/s)	effective Pe_m	$D \times 10^5$ (cm ² /s)
	0.0854	1.00×10^{-5}	6.91×10^{-5}	4.93×10^{-5}	0.700	1.49
	0.222	2.60×10^{-5}	1.80×10^{-4}	1.28×10^{-4}	1.82	1.55
	0.854	1.00×10^{-4}	6.91×10^{-4}	4.93×10^{-4}	7.00	2.26

In all cases, the value of the simulated diffusivity increased with increasing effective Pe_m (i.e., with increasing temperature difference, and, thus, convective velocity magnitude). The dependence of the transport conditions on the nature of the thermal boundary conditions was such that for a uniform heat flux along the sidewall which produces a radial temperature difference in the liquid, the diffusivity vs. Pe_m were indistinguishable for $Ha = 25$ and 100. The diffusivities for $Ha = 100$ were higher than those for $Ha = 25$ in the presence of a periodic temperature profile produced by a periodic heat flux superimposed on a uniform heat flux (Cases II, III, IV, and V).

Case I which is uniform heat flux only (i.e., the radial temperature difference in the liquid is the only driving force) seems to be the most sensitive while Case V is the least sensitive among five different conditions considered in this model. From the results, one can conclude that a particular temperature profile at the sidewall (produced by a combination of uniform and non-uniform heat fluxes) is required to result in desired diffusivities (i.e., to operate within the allowable temperature non-uniformities) in self-diffusion experiments for this numerical model. For a fixed value of effective Pe_m , ΔT_r increases with increasing Ha (the magnetic field strength). Thus, stronger magnetic fields can tolerate a stronger driving force ΔT_r in self-diffusivity measurements for same convective conditions.

Acknowledgements

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THERMOPHYSICAL PROPERTIES OF Te-BASED II-VI SEMICONDUCTORS: REDUCED ALGORITHMS FOR THERMAL DIFFUSIVITY DETERMINATION

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Abstract

This paper presents methodologies for measuring the thermal diffusivity using the difference between temperatures measured at two, essentially independent, locations. A heat pulse is applied for an arbitrary time to one region of the sample; either the inner core or the outer wall. Temperature changes are then monitored versus time. The thermal diffusivity is calculated from the temperature difference versus time. No initial conditions are used directly in the final results.

I. Introduction

The determination of the thermal diffusivity κ (or conductivity k) typically requires precise knowledge of the applied parameters. Such parameters include the time at which a heat pulse was applied, the amount of energy added or the initial temperature increase. The diffusivity is then obtained by matching the experimentally measured profile to the output of an analytical/numerical model. The resulting diffusivity is sensitive to values of these applied parameters.

In most circumstances, measuring thermal diffusivities in liquids is complicated by convection that occurs in the sample due to the applied temperature gradient. See [1,2] for a discussion of convective flows due to density gradients in a gravitational field. In metals, which have relatively high values of κ , this convective contribution will typically be less than a percent. However, for low thermal conductivity liquids, e.g., the II-VI semiconductors, convective heat transport may be important relative to heat conduction. Earlier studies have confirmed the advantage of making such measurements in a low-gravity environment [3]. We plan to measure the thermal diffusivity of molten II-VI semiconductors, for which convective contamination in the data is expected. Therefore, we are looking for a methodology that is efficient and simple for conducting measurements of thermal diffusivities in orbiting spacecraft.

In general, this paper presents a methodology for measuring the thermal diffusivity using the difference between the temperatures measured at two locations in cylindrical samples. We have developed algorithms that allow us to use either heating of the center portion of the sample or the samples edge. The final form of the equation used to calculate the thermal diffusivity is the same for either heating scheme. For both heating geometries the heat pulse is applied for an arbitrary. Temperature changes are then monitored versus time and the thermal diffusivity is calculated from the temperature differences only versus time. No initial conditions are used directly in the final result.

Keywords: thermal diffusivity, thermal conductivity, flight

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In section II-A of this paper, we describe the mathematical formulation of the problem for central region heating. In section II-B we briefly describe the mathematical formulation of the problem for edge heating. Then by means of numerical simulations we examine the effect of variations in the heated region area and measurement locations (Sec. II-C and D). Finally, in Sec. II-E we examine our analytical solution to explain why these effects make such a small difference in the results, considering the stringent conditions that we started with. Section III covers our experimental set-up and results for fine-grained graphite and boron nitride.

II. Temperature In A Cylindrical Rod: The General Problem

II-A Mathematical Formulation for Central Region Heating

We consider a perfectly insulated circular cylinder under conditions for which the temperature depends only on the cylindrical radius r . The initial temperature distribution is $T(r, 0) = f(r)$ given by

$$f(r) = \begin{cases} T_0 & \text{for } 0 < r/a < p \\ 0 & \text{for } p < r/a < 1 \end{cases} \quad (1)$$

where $0 < p < 1$; a is the cylinder radius, and T_0 is a constant, see Fig. 1. For time $t > 0$, radial heat transfer begins.

The evolution of the temperature $T(r, t)$ is then given [4] by the expression

$$T(r, t) = \frac{2}{a^2} \left(\int_0^a r f(r) dr + \sum_{n=1}^{\infty} \exp(-\kappa \alpha_n^2 t) \frac{J_0(r \alpha_n)}{J_0^2(a \alpha_n)} \int_0^a r f(r) J_0(\alpha_n r) dr \right) \quad (2)$$

where $\mu_n = a \alpha_n$ is the n^{th} positive root of the Bessel function of the first kind of order 1, i.e., $J_1(\mu_n) = 0$. Using the initial conditions defined above, and after several substitutions the integrals in Eq. (2) become

$$T(r, t) = T_0 p^2 + T_0 \sum_{n=1}^{\infty} \exp\left(\frac{-\kappa \mu_n^2 t}{a^2}\right) \frac{2p}{\mu_n} \frac{J_0(\mu_n r/a)}{J_0^2(\mu_n)} J_1(\mu_n p) \quad (3)$$

We shall proceed to simplify the infinite sum in Eq. (3) by eliminating the $n = 2$ and $n = 3$ terms. Since the terms for $n > 3$ decay rapidly with time, we will be left after a short transient with $n = 1$ term, **a tractable expression that can be used to analyze experimental data**. Setting p , the ratio of the heated to the sample radius, equal to the special value $\mu_1/\mu_2 = 0.5436$, we can eliminate the $n = 2$ term of the series because

$$J_1(\mu_2 p) = J_1(\mu_1) = 0. \quad (4)$$

The $n = 3$ term can be set to zero by choosing the temperature measurement locations r so that $\mu_3 r/a = v_n$ corresponds to the first three zeros of J_0 , i.e., $J_0(v_n) = 0$, which are 2.4048, 5.5201 and 8.6537, respectively. With $\mu_3 = 10.17347$, this results in three special values of r given by $r_1/a = v_1/\mu_3 = 0.2364$, $r_2/a = v_2/\mu_3 = 0.5426$, and $v_3/\mu_3 = 0.8506$. The next zero of J_0 is at $v_4 = 11.792$ and would result in a value $r_4/a > 1$, outside the sample.

The geometry of the heated area and the three special values of r (temperature measurement locations for the experiments) are shown in Fig. 1. With the $n = 2$ and $n = 3$ terms set to zero by means of the choices adopted above, the temperature at each r_i is,

$$T(r_i, t) = T_0 p^2 + T_0 \frac{2p}{\mu_1} \frac{J_0(\mu_1 r_i/a)}{J_0^2(\mu_1)} J_1(\mu_1 p) \exp\left(\frac{-\kappa \mu_1^2 t}{a^2}\right) + h.o.t. \quad (5)$$

where h.o.t. stands for higher order terms having $n > 3$.

Taking the difference between two locations, for example between r_1 and r_3 ,

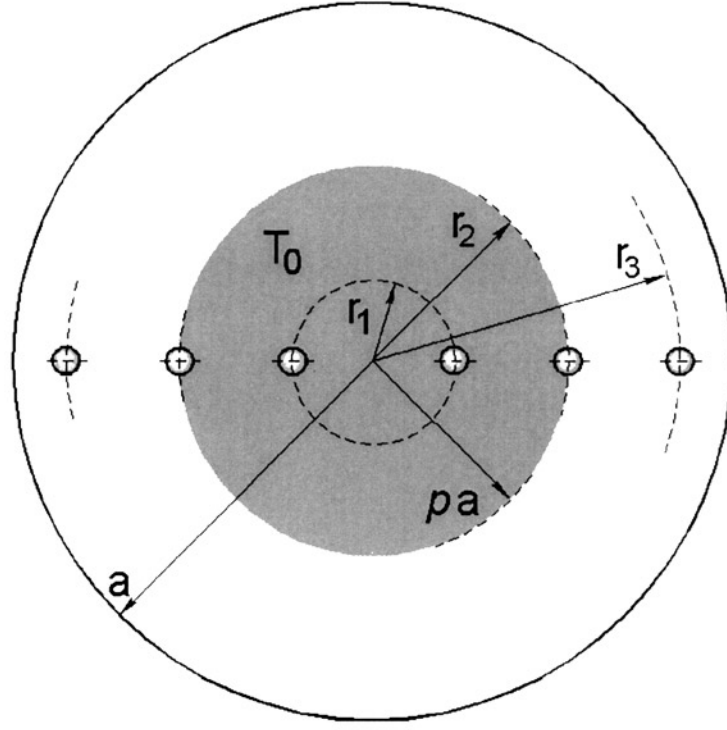


Fig. 1 Plan view of the sample showing the positions of the heated region and temperature measurement locations for central heated region.

$$T(r_1, t) - T(r_3, t) = T_0 \frac{2p}{\mu_1} \frac{J_1(\mu_1 p)}{J_0^2(\mu_1)} \left(J_0\left(\mu_1 \frac{r_1}{a}\right) - J_0\left(\mu_1 \frac{r_3}{a}\right) \right) \exp\left(\frac{-\kappa \mu_1^2 t}{a^2}\right) + \Delta(h.o.t.) \quad (6)$$

It can be shown that the difference between the higher order terms in Eq. (6) is less than 1% of the $n = 1$ term for $\kappa t/a^2 > 0.015$. This corresponds to a time greater than 3.7 s for $a = 5$ cm and $\kappa = 0.1$ cm²/s. The effects of this condition will be discussed in section II-C. Neglecting such high order terms, and taking the natural logarithms of the differences $\Delta T_{ij} = T(r_i, t) - T(r_j, t)$, we obtain

$$\ln(\Delta T_{ij}) = \ln(\beta_{ij}) - \left(\frac{\kappa \mu_1^2}{a^2}\right) t \quad (7)$$

where

$$\beta_{ij} = T_0 \frac{2p}{\mu_1} \frac{J_1(\mu_1 p)}{J_0^2(\mu_1)} \left(J_0\left(\mu_1 \frac{r_i}{a}\right) - J_0\left(\mu_1 \frac{r_j}{a}\right) \right). \quad (8)$$

Details of all of the initial conditions, including the initial applied temperature T_0 , are contained in β_{ij} . Therefore, the slope of a plot of $\ln(\Delta T_{ij})$ versus t is independent of the details of the initial conditions and is proportional to the value of κ , with a known proportionality constant.

The values of thermal diffusivity are obtained from the slopes of the curves of $\ln(\Delta T_{ij})$ as a function of time, as shown in Fig. 2. Note that the resulting diffusivity depends only on the slope of the curve, i.e., we have met the requirement that no knowledge of initial conditions are necessary for the final analysis.

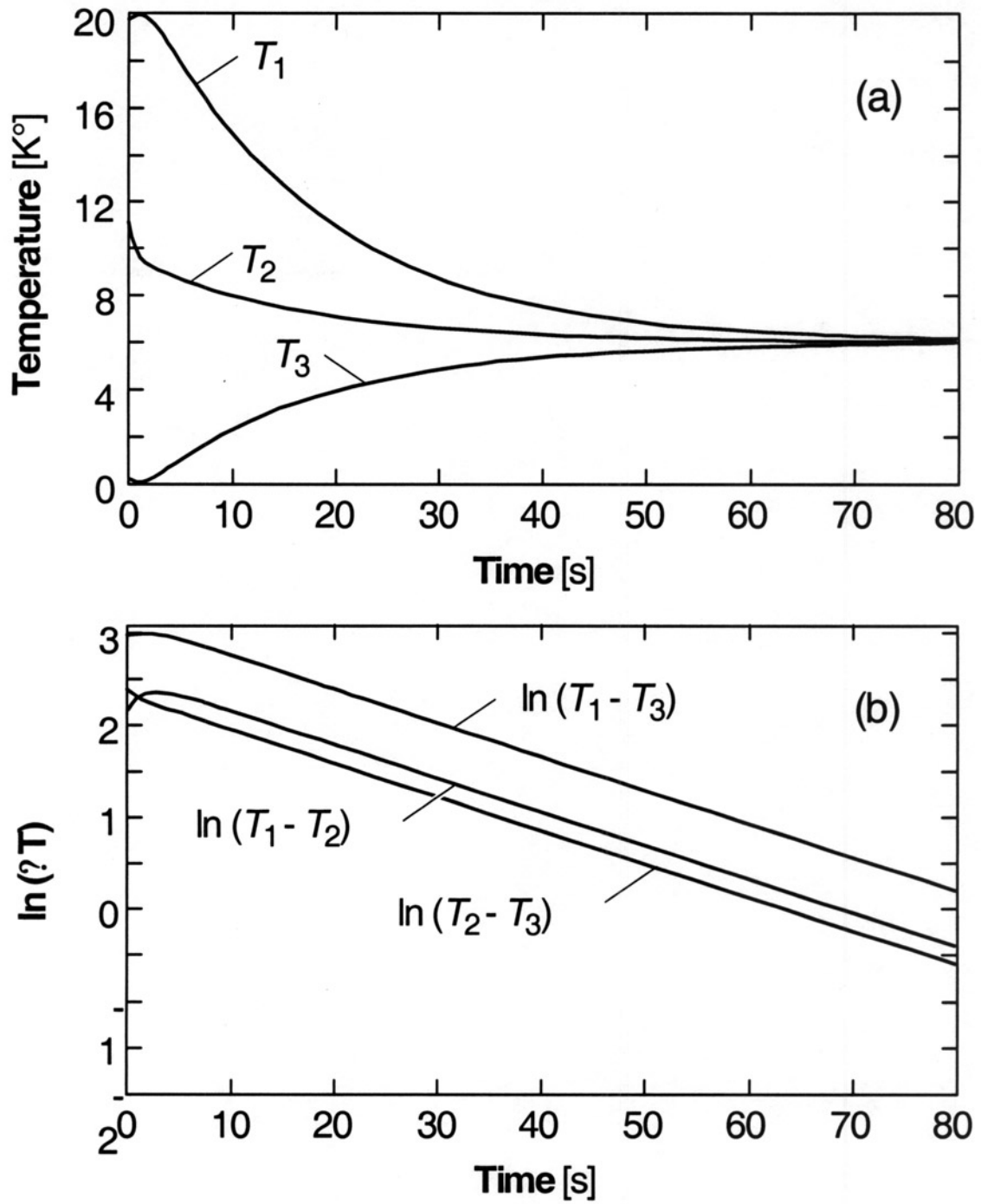


Fig. 2 Temperature profiles and values of $\ln(\Delta T_{ij})$ versus time, generated numerically by using the special heated region and measurement locations. The thermal diffusivity was $0.1 \text{ cm}^2/\text{sec}$. T_i is the temperature at special measurement location r_i .

II-B Mathematical Formulation for Outside Edge Heating

In a similar vein to the final equation derived above for central region heating we arrive at a similar equation for edge heating. We again consider a perfectly insulated cylinder under conditions for which the temperature depends only on the radius r . The initial conditions are, initial temperature T_0 throughout the cylinder and, a heat flux Q'' is applied to the surface for a time $0 \leq t \leq t_e$. The heat flux initial condition (at $r = R$) is expressed as:

$$\text{at } r = R: -K \frac{\partial T}{\partial r} = Q'' [1 - h(t - t_e)] \quad (9)$$

where the function h is the Unit Step or Heaviside function, and K the thermal conductivity.

The evolution of the temperature as a function of position and time $T(r, t)$ is obtained by solving the transient form of the heat equation in cylindrical coordinates.

$$\frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} = \frac{1}{\kappa} \frac{\partial T}{\partial t} \quad (10)$$

The solution is:

$$f = -\frac{Q'' R}{K} \left\{ \frac{2\kappa t}{R^2} + \frac{r^2}{2R^2} - \frac{1}{4} - 2 \sum_{s=1}^{\infty} e^{-\frac{\kappa \alpha_s^2 t}{R^2}} \frac{J_0\left(\frac{r \alpha_s}{R}\right)}{\alpha_s^2 J_0(\alpha_s)} \right\} \quad (11)$$

where α_s are the positive roots of $J_1(\alpha) = 0$. [Caslaw and Jeager, Conduction of Heat in Solids, 2nd edition, p 329] Taking the result from Carslaw and Jaeger, it is important to note, that their initial condition is $T_0 = 0$. To have a more general case, the initial value T_0 of the temperature is added to this result.

The presence of the Heaviside function in the solution, divides this problem into two cases, one for $t \leq t_e$ during the heating, and one for $t > t_e$ after the pulse is turned off.

We are interesting in the cooling phase only which yields for the temperature distribution:

$$T(r, t) = -\frac{Q'' R}{K} \left\{ \frac{2\kappa t_e}{R^2} - 2 \sum_{s=1}^{\infty} \left[e^{-\frac{\kappa \alpha_s^2 t}{R^2}} \left(1 - e^{-\frac{\kappa \alpha_s^2 t_e}{R^2}} \right) \right] \frac{J_0\left(\frac{r \alpha_s}{R}\right)}{\alpha_s^2 J_0(\alpha_s)} \right\} + T_0 \quad (12)$$

Only the $n=2$ term can be set to zero, by choosing the temperature measurement locations r_i , in this heating geometry. This is done by setting the $r \alpha_s / R = \nu_n$ terms to the first two zeros of J_0 , or at $J_0(\nu_n) = 0$ at $\nu_n = 2.4048$ and 5.5201 . With $\alpha_2 = 7.01559$ the measurement locations are then set at

$$\frac{r_1}{R} = \frac{\nu_1}{\alpha_2} = 0.342779 \text{ and } \frac{r_2}{R} = \frac{\nu_2}{\alpha_2} = 0.786833.$$

Other terms cannot be so eliminated, however, terms for $n \leq 3$ decay rapidly with time in comparison to the first two terms. Grouping the $n \leq 3$ terms together as higher order terms yields

$$T(r, t) = -\frac{Q'' R}{K} \left\{ \frac{2\kappa t_e}{R^2} - 2 \left[e^{-\frac{\kappa \alpha_1^2 t}{R^2}} \left(1 - e^{-\frac{\kappa \alpha_1^2 t_e}{R^2}} \right) \right] \frac{J_0\left(\frac{r \alpha_1}{R}\right)}{\alpha_s^2 J_0(\alpha_1)} \right\} + h.o.t. \quad (13)$$

Taking the temperature difference between two locations, T_i and T_j :

$$T(r_i, t) - T(r_j, t) = -\frac{Q'' R}{K} \left\{ \left[-2 \left[e^{-\frac{\kappa \alpha_1^2 t}{R^2}} \left(1 - e^{-\frac{\kappa \alpha_1^2 t_e}{R^2}} \right) \right] \frac{J_0\left(\frac{r_i \alpha_1}{R}\right) - J_0\left(\frac{r_j \alpha_1}{R}\right)}{\alpha_s^2 J_0(\alpha_1)} \right] \right\} + \Delta h.o.t \quad (14)$$

This reduces to:

$$T(r_i, t) - T(r_j, t) = e^{-\frac{\kappa \alpha_1^2 t}{R^2}} \times \frac{2Q'' R}{K} \left(1 - e^{-\frac{\kappa \alpha_1^2 t_e}{R^2}} \right) \frac{J_0\left(\frac{r_i \alpha_1}{R}\right) - J_0\left(\frac{r_j \alpha_1}{R}\right)}{\alpha_s^2 J_0(\alpha_1)} \quad (15)$$

Then taking the natural logarithm of the difference we arrive at a solution analogous to equation (7) above:

$$\ln(\Delta T_{ij}) = -\frac{\kappa \alpha_1^2}{R^2} t + \ln(\beta_{ij}) \quad (16)$$

Thus, for either heating geometry we arrive at a solution where only the measured temperature difference versus time is required to calculate the thermal diffusivity.

II-C Modification of the Heated Region-Central Region Heating

We investigate the effect of varying the size of the heated region on the output diffusivity. Initially, this work was intended to see how much error could be tolerated in the heated area; recall that our derivation is based on a special value $p = 0.546$, leading to elimination of the $n = 2$ term in Eq. (5). Here again, we show the results for $\kappa = 0.1 \text{ cm}^2/\text{sec}$; the results for the other values of κ follow with linear time scaling. The sample radius for these cases was 5 cm, so the special value of p corresponds with a radius of the heated region of 2.73 cm. Two, extreme, cases are shown here; 1) when the heated region is increased to 125% of the special radius, and 2) decreased to 20%. Thus, the radii of the heated regions considered here are 3.41, and 0.556 cm, respectively.

The temperature increase at equilibrium is given by $T_0 p^2$. Therefore, for an initial temperature of 20 K, the final temperature increases for the exact solution and the two modified cases are expected to be 6.0, 9.3 (125%), and 0.2°C (20%), respectively. The effect of these values on the experimental diffusivity was mentioned before and will be further discussed below.

Figs. 3a, and 4a show a plot of the temperature versus time at the three measurement locations for the modified heated radii (125%, and 20% respectively). These can be compared with Fig. 2 which shows the temperature versus time for the heated region of special radius. The effect of changing the size of the heated region on the measured temperature at r_2 is obvious in Figs. 3a, 4a. Note that for the 0.5 cm heated region (20% of the special p value) the initial T_0 is not seen in the plot since there is no measurement location within this area, Fig. 4a. This change follows what would be intuitively expected, i.e., for the larger heated region, $T(r_2, t)$ is higher, while it is lower for the 20% case (i.e., $p = 0.11$ case). **Note that the approximate time to reach equilibrium is not changed.**

The corresponding plots of $\ln(\Delta T)$ versus time are shown in Figs. 3b, and 4b. Comparing Fig. 2a (special p), at the shorter times, with the modified cases shows the effect of the $n = 2$ term being non-zero on the development of the curve. In Fig. 2b the plot of $\ln(\Delta T)$ versus time becomes linear after about $t > 5$ sec. In Fig. 3b, and 4b, it is not until about 10 seconds that the plots become linear and the input diffusivity is

recovered. For the 125 % case, the time period over which the plot is linear is approximately the same as for the special p case and corresponds to the original diffusivity value to within 1%.

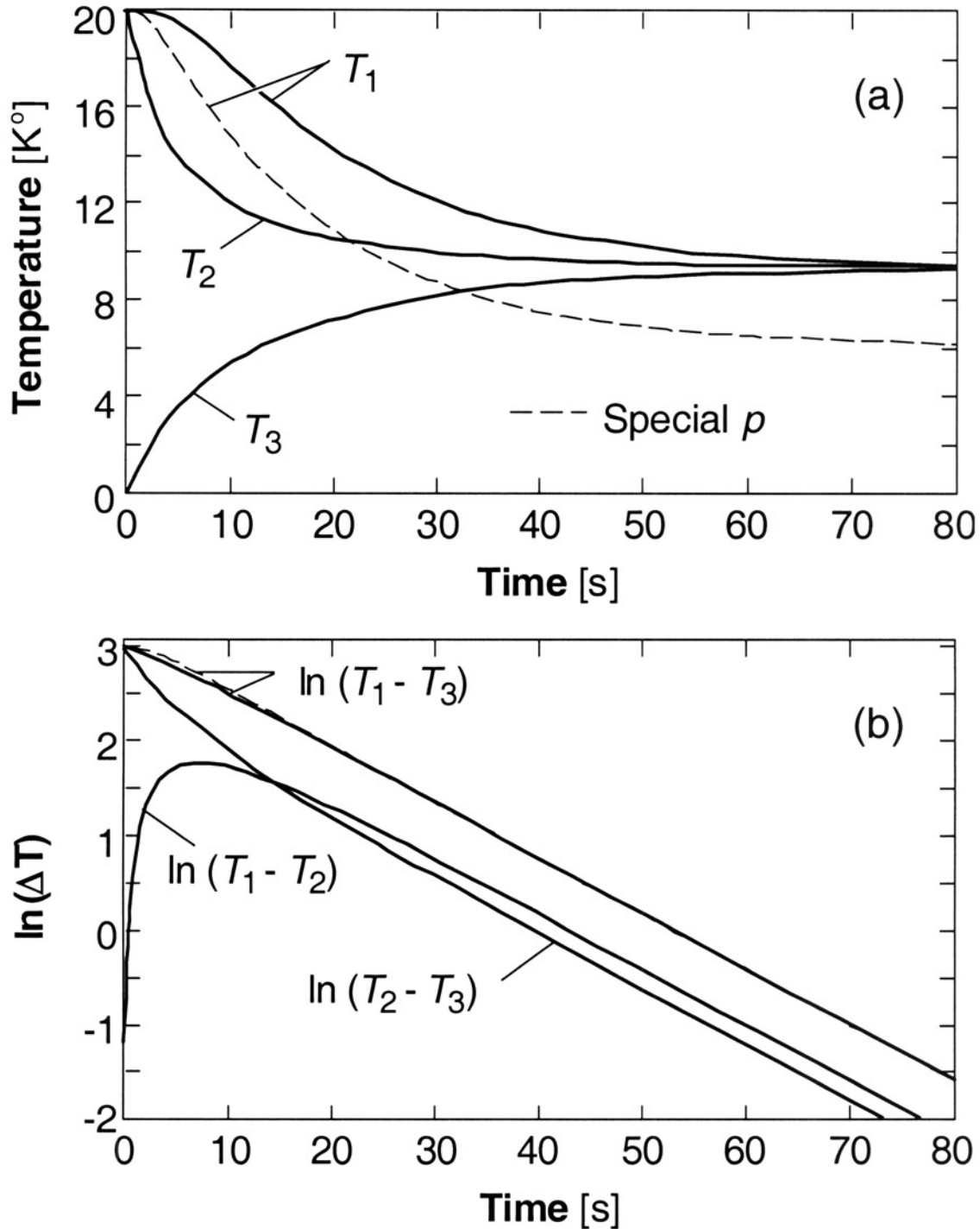


Fig. 3 Temperature profiles and values of $\ln(\Delta T_{ij})$ versus time, generated numerically by using a heated radius 125% larger than the special value and the special measurement locations with no noise. Notice the increase in the temperatures versus time compared to Fig. 2. Figure (b) shows that longer time is required before the diffusivity can be extracted due to the fact that r_2 is no longer at the edge of the boundary between the heated and unheated regions.

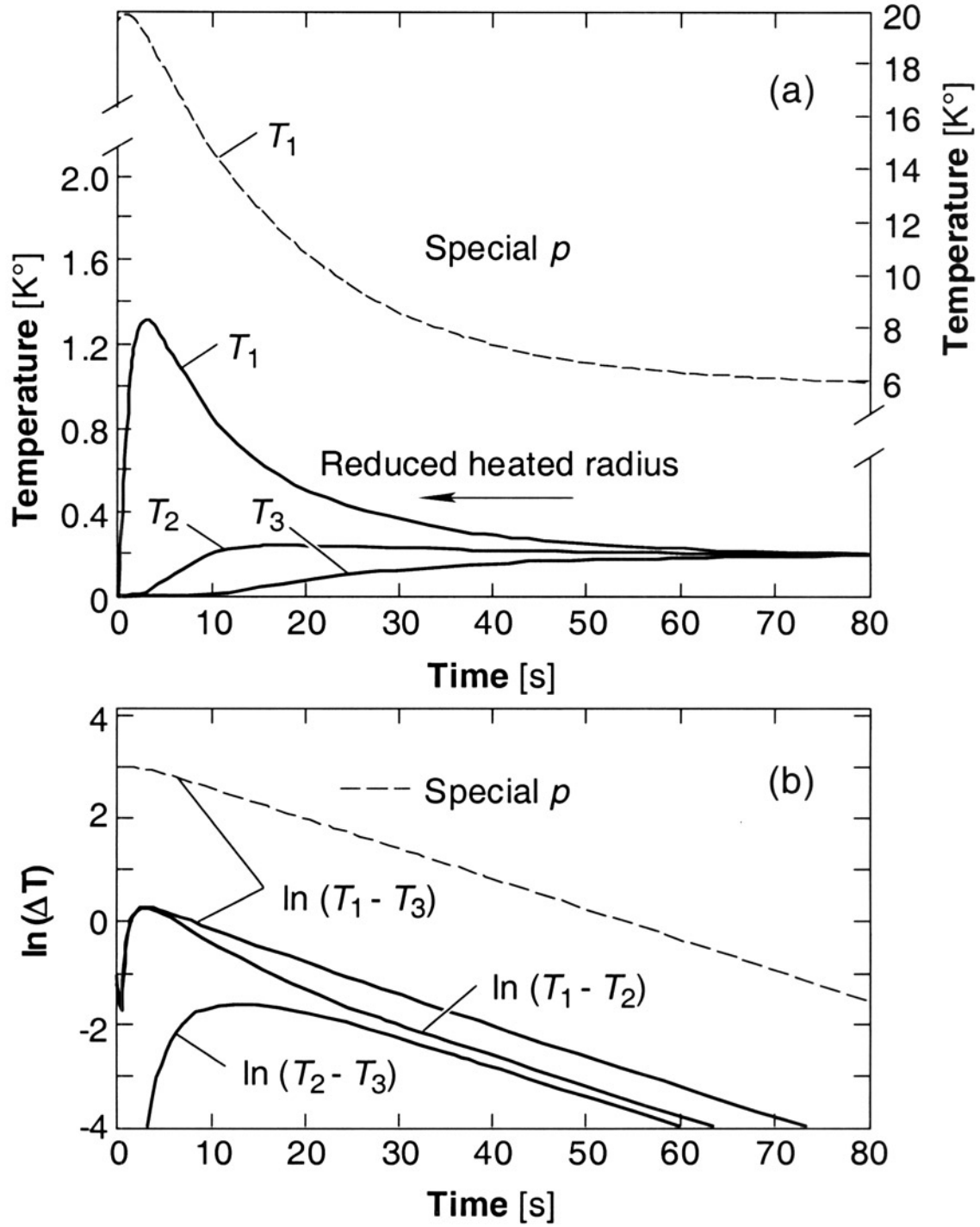


Fig. 4 Temperature profiles and values of $\ln(\Delta T_{ij})$'s versus time generated numerically by using a heated region of size 20% of special value and the special measurement locations with no noise. Note the very small increase in T_1 since the heated region is inside this measurement location. Due to the low values of ΔT the thermal diffusivity can only be extracted from $\ln(\Delta T_{13})$.

II-D Variations in Measurement Locations

The effect of variations in the measurement locations is essentially the same as that for modifications in the heated region, i.e., at long enough times the effect is negligible. This can be seen from Fig. 5a and 5b. Fig. 5 shows the evolution of the temperature profile and $\ln(\Delta T)$ versus time for r_1, r_2 and r_3 of 0.1, 2.5 and, 4.9 cm, (the special r_i values are 1.182, 2.71 and 4.253 cm for $a = 5.0$ cm). As in the above cases, after 10

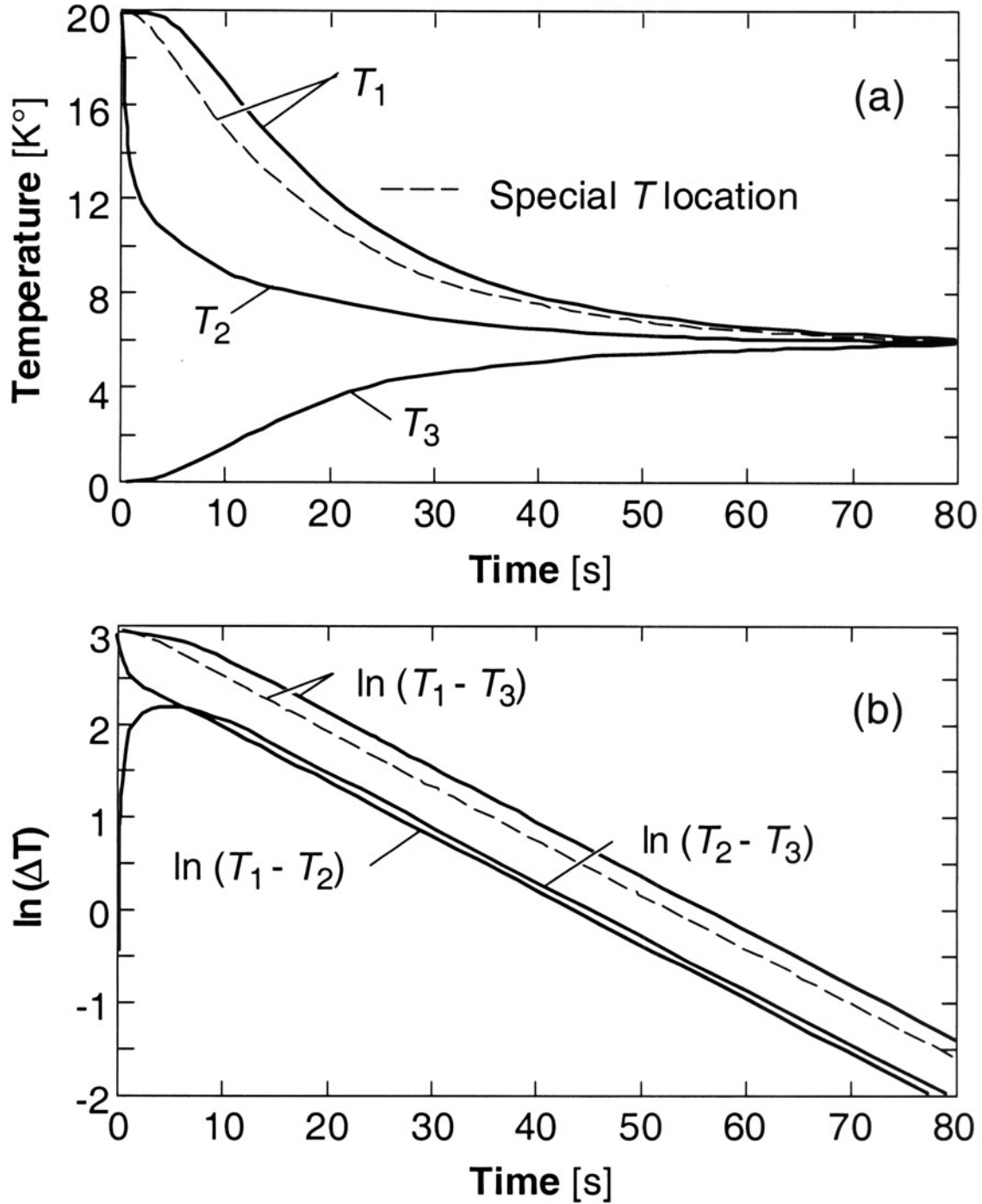


Fig. 5 Temperature profiles and values of $\ln(\Delta T_{ij})$'s versus time generated numerically by using a heated region of the special size and the modified measurement locations. T_1 and T_3 are inside and outside the correct positions. (b) Longer time is require before the diffusivity can be extracted.

seconds the original diffusivity values are returned. The difference in the temperature profiles at r_1 , r_2 and r_3 between a solution containing 20 terms and a solution containing the constant term $T_0 p^2$ and the $n = 1$ term is less than 0.01 % for values of the non-dimensional coefficient $\kappa t/a^2$ greater or equal than 0.04.

Conclusions

We have developed novel methodology(ies) for measuring thermal diffusivities. This methodology does not require knowing the initial temperature increase or any timing between the applied and measured response. We have shown by numerical simulation that a relative imposed error up to 10% can be tolerated. We have proven that it is possible to extract an accurate value of thermal diffusivity when the heated region is reduced up to 20% of the special value needed to simplify the analytical series solution. Increasing the initial temperature and using modified measurement locations is helpful. Finally, by scaling analysis we have a measure of the time when the thermal diffusivity values are reliable.

Acknowledgements

Financial support for this work by the Microgravity Sciences and Application Division of the National Aeronautics and Space Administration, through grant NAG8-1476, is gratefully acknowledged. RFS is also grateful for support from NASA grant NAG8-1704. We thank Lynne Carver for expert preparation of the figures.

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THE SOLIDIFICATION VELOCITY OF UNDERCOOLED NICKEL AND TITANIUM ALLOYS WITH DILUTE SOLUTE

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Introduction

The study of solidification velocity is important for two reasons. First, understanding the manner in which the degree of undercooling of the liquid and solidification velocity affect the microstructure of the solid is fundamental. Second, there is disagreement between theoretical predictions of the relationship between undercooling and solidification velocity and experimental results.

Thus, the objective of this research is to accurately and systematically quantify the solidification velocity as a function of undercooling for dilute nickel- and titanium-based alloys. The alloys chosen for study cover a wide range of equilibrium partition coefficients, and the results are compared to current theory.

The IMS Model

Boettinger, Coriell, and Trivedi¹ formulated one of the most widely used models for describing the nature of the solidification velocity of undercooled metal systems. The model combines the Ivantsov² solution for the diffusional fields about a paraboloid of revolution with the marginal stability arguments of Langer and Müller-Krumbhaar³ and non-equilibrium interface conditions as determined by Aziz and Kaplan^{4,5}. Together, they form what is referred to as the BCT theory or IMS model for rapid solidification. The model predicts solidification velocity as a function of undercooling for dilute alloys.

Boettinger et al¹ give the total undercooling, ΔT , as

$$\Delta T = \left(\frac{L}{C} \right) Iv(P_t) + m_L C_o \left[1 - \frac{m'_L / m_L}{1 - (1-k) Iv(P_c)} \right] + \frac{2T_m \Gamma}{r} + \frac{RT_m^2}{L} \frac{V}{V_o} \quad (1)$$

where L is the latent heat of fusion, C is the heat capacity, $Iv(x)$ is the Ivantsov function, m_L is the liquidus slope, C_o is the alloy concentration, T_m is the melting temperature, Γ is the Gibbs-Thomson coefficient (ratio of interfacial energy, σ , to the entropy of fusion), r is the dendrite tip radius, R is the gas constant, V is the dendrite tip velocity, and V_o is the speed of sound in the liquid. The thermal and solutal Peclet numbers, P_t and P_c respectively, are given as

$$P_t = \frac{Vr}{2\alpha} \quad (2)$$

and

$$P_c = \frac{Vr}{2D} \quad (3)$$

where α is the thermal diffusivity and D is the solutal diffusivity. The partition coefficient, k , is given as

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$$k = \frac{k_E + \beta_0 V}{1 + \beta_0 V} \quad (4)$$

where k_E is the equilibrium partition coefficient. The solute trapping kinetic parameter, β_0 , is given as

$$\beta_0 = \frac{a_0}{D} \quad (5)$$

where a_0 is the diffusive length scale. The effective liquidus slope, m_L' is given as

$$m_L' = m_L \left[1 + \frac{k_E - k \left(1 - \ln \frac{k}{k_E} \right)}{1 - k_E} \right] \quad (6)$$

The marginal stability criterion is used to decouple V and r , since they are not uniquely specified by the equation 1. The dendrite tip radius, r , is given as

$$r = \frac{T_m \Gamma / \sigma^*}{\left(\frac{L}{C} \right) P_t \xi_t + \frac{2m_L C_o (k-1)}{1 - (1-k) Iv(P_c)} \xi_c} \quad (7)$$

where

$$\xi_t = 1 - \frac{1}{\sqrt{1 + (\sigma^* P_t^2)^{-1}}} \quad (8)$$

and

$$\xi_c = 1 + \frac{2k}{1 - 2k - \sqrt{1 + (\sigma^* P_c^2)^{-1}}} \quad (9)$$

The marginal stability parameter, σ^* , is often taken to be¹ a constant equal to $(4\pi^2)^{-1}$.

The IMS model predicts an increase in solidification velocity with increasing undercooling at low undercoolings. In this low undercooling regime, dendrite growth is solutally controlled. Eventually, the curve reaches a plateau, and then rapidly increases during a transition to thermally controlled growth accompanied by solute trapping.

The prediction of the solidification velocity by the IMS model depends on the selection of thermophysical properties used in the calculations. Of the thermophysical properties in the model, the following parameters are reasonably well known for a given alloy: T_m , L , C , m_L , C_o , k_E , and V_o . The remaining parameters are equivocal and are known within an order of magnitude: D , a_0 , α , and σ . In general for most metals, D is on the order of 10^{-9} to 10^{-8} m²/s, a_0 is on the order of 10^{-10} to 10^{-9} m, α is on the order of 10^{-6} to 10^{-5} m²/s, and σ is roughly 0.15 to 0.35 J/m². Because of the uncertainty associated with these equivocal parameters, these variables can be “adjustable” in the model to determine if IMS modeling will fit experimental results.

In order to test the sensitivity of the IMS model to variations in the equivocal parameters, calculations were made by adjusting one equivocal variable of interest while holding all others constant. The parameters used for the sensitivity analyses are shown in table 1, and the results are shown in figure 1. Due to the small

numerical range of interfacial energy and its limited effect on the overall shape of the solidification velocity versus undercooling curve, the effect of varying σ is not a main consideration for sensitivity analysis.

Using a dilute nickel-based alloy (1% solute), the effect of varying β_0 is shown in figure 1a. This shows that the velocity at which the plateau appears increases with decreasing β_0 . This is expected since faster diffusing species (or shorter diffusional length scales) would cause the solidification velocity plateau to appear at higher velocities. In figure 1a, β_0 was varied by holding D constant while varying a_0 . An equivalent analysis may be conducted by holding a_0 constant while varying D . This would result in curves that although may be numerically different than figure 1, would exhibit the same relationship between plateau velocity and β_0 .

The effect of varying α is shown in figure 1b. The solidification velocity is decreased at higher undercoolings with decreasing thermal diffusivity. Since the higher undercooling regime involves thermally controlled growth, lower thermal diffusivities will cause slower solidification velocities. Lower thermal diffusivities also damp the appearance of a velocity plateau, as the transition from solutally controlled growth to thermally controlled growth becomes indistinguishable with respect to its velocity. Thus, figure 1b also demonstrates that certain values for the IMS model parameters could describe a set of conditions such that a transition in growth behavior would not manifest itself in plateaus or other abrupt changes in the solidification velocity versus undercooling curve. Another possibility is that solidification velocity is entirely dominated by one growth behavior or another for certain values of IMS model parameters. In these cases, the curve would appear to be smooth and closely approximate a parabolic or power law.

The solute species in an alloy determines k_E and m_L for the IMS model calculation; these variables are reasonably well known for a given alloy system. The sensitivity analysis in figure 1c shows how the solidification velocity versus undercooling curve changes as a function of solute species. Figure 1c shows the effect of varying k_E and illustrates that the plateau in solidification velocity is damped for large values of k_E . Because large k_E alloys are predicted to exhibit weak partitioning across the solid-liquid interface during solidification, the IMS model does not contain a noticeable plateau in the solidification velocity versus undercooling curve. Thus, the IMS model predicts that the solidification velocity plateau should only appear for small k_E alloys. For most metals, m_L has a range of approximately -2 to $-30\text{K/at\%}$. While the value of m_L has large quantitative effects on the IMS model, the shape of the solidification velocity versus undercooling curve is not greatly affected. As predicted by the IMS model, small k_E alloys have a pronounced solidification velocity plateau, while large k_E alloys do not regardless of the value of m_L .

Table 1: IMS model parameters used in numerical sensitivity analysis for a dilute nickel-based alloy in figure 1.

	Effect of varying solute trapping kinetic parameter in figure 1a	Effect of varying thermal diffusivity in figure 1b	Effect of varying equilibrium partition coefficient in figure 1c
T_m (K)	1726	1726	1726
L (J/mol)	17120	17120	17120
C (J/molK)	43	43	43
k_E	0.005	0.2	Variable
a_0 (m)	Variable	2×10^{-10}	7×10^{-10}
m_L (K/at%)	-10.6	-10.6	-10.6
C_0 (at%)	1	1	1
α (m ² /s)	10^{-5}	Variable	10^{-5}
D (m ² /s)	7×10^{-9}	7×10^{-9}	7×10^{-9}
V_0 (m/s)	4036	4036	4036
σ (J/m ²)	0.23	0.23	0.23

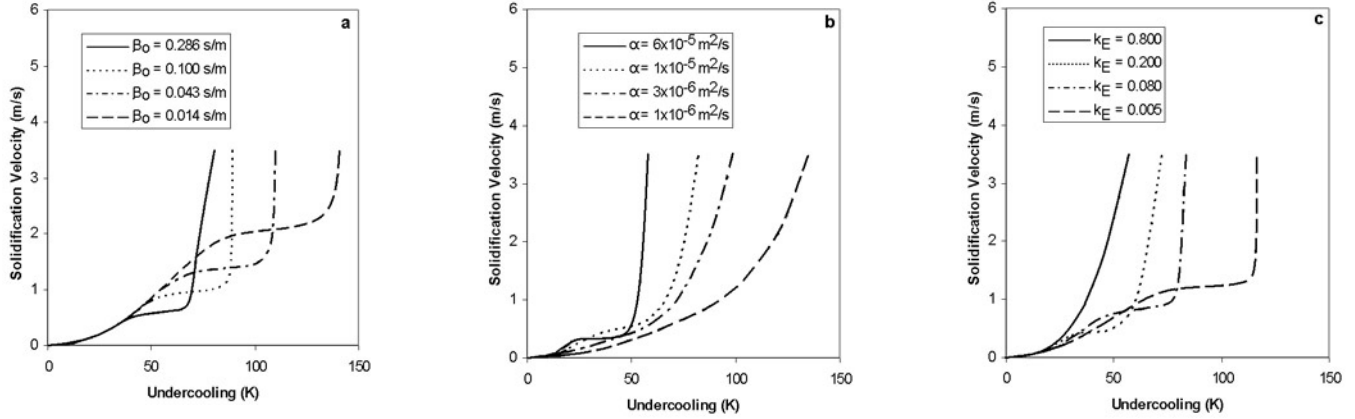


Figure 1: Sensitivity analysis of IMS model with one parameter varied while all others held constant. Variable parameters: (a) solute trapping kinetic parameter, β_0 , with D held constant and a_0 varied, (b) thermal diffusivity, α , and (c) equilibrium partition coefficient, k_E .

The Effect of Oxygen in Pure Metals

There is disagreement between theory and experimental results as well as wide data scatter between various experimenters in ground-based research efforts. The solidification velocity of pure nickel was measured by several experimenters⁶⁻¹³, and the results are shown in figure 2. This composite plot shows that at undercoolings less than 10% of the melting temperature, T_m , solidification velocity is observed as increasing for increasing undercooling. At undercoolings greater than 10% T_m , there is wide divergence in solidification velocity results. At the upper limit of solidification velocity, Walker et al⁶ show a continuously increasing velocity with increasing undercooling, while the results of Bassler et al⁹ show a velocity plateau at high undercoolings.

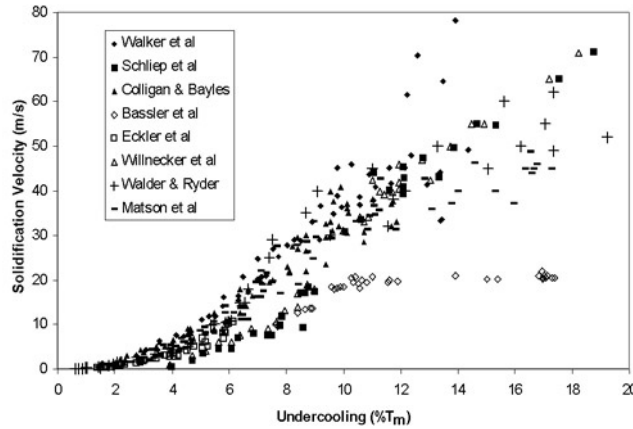


Figure 2: Solidification velocity of pure nickel as measured by several experimenters⁶⁻¹³.

Bassler¹⁴ and Walder and Ryder¹² measured the solidification velocity of pure titanium as a function of undercooling, and the results are shown in figure 3. Both studies show a continuous rise in solidification velocity with increasing undercooling.

Bassler¹⁴ measured the solidification velocity of pure nickel in three different processing environments: He- H_2 , UHP He, and with an air leak in the system. The results are shown in figure 4. The different

environments were used to determine the effect of oxygen on the solidification of pure nickel. He-H₂ was used as an oxygen-reducing environment, while the UHP He and air leak environments increased the oxygen content in the system during processing. The results show that for low oxygen environments, the solidification velocity of pure nickel increases with increasing undercooling until reaching a velocity plateau at high undercooling. Solidification velocities as a function of undercooling were lower for samples processed in the UHP He environment, but velocity also increases until reaching a plateau at high undercooling. Finally, for those samples processed with an air leak in the system, solidification velocity was markedly suppressed for the entire range of undercoolings.

Cochrane et al¹⁵ measured the solidification velocity of pure copper for one set of samples containing approximately 10ppm oxygen and another set of samples containing an average concentration of approximately 600ppm oxygen. The results are shown in figure 5 along with the theoretical prediction of Lipton, Kurz and Trivedi¹⁶ (LKT theory). For the samples with a higher oxygen concentration, solidification velocities are lower than those for the low oxygen concentration samples. Additionally, these higher oxygen concentration samples deviate from theory above 200K undercooling.

Obviously, figures 2 through 5 illustrate the effects of oxygen on the solidification velocity of pure metals. In “pure” nickel and “pure” copper, residual oxygen reduces solidification velocities at all undercoolings and depending on concentration, produces a plateau in solidification velocity at high undercoolings. In “pure” titanium, no plateau in solidification velocity is reached at high undercoolings.

Experimental Method

Solidification velocity measurements of undercooled melts are accomplished in Vanderbilt’s electromagnetic levitator. Containerless processing by electromagnetic levitation allows for large degrees of undercooling to be readily achieved, and allows for direct observation of the sample surface during recalescence. Thermal imaging techniques are used to capture the recalescence event, while optical pyrometry is used to measure bulk temperature. A schematic diagram of Vanderbilt’s electromagnetic levitator is shown in figure 6.

Two means of thermal imaging are utilized in solidification velocity measurements. For low undercoolings ($<5\%T_m$), a Dalsa digital CCD camera is used. The Dalsa camera is an 8-bit camera with 64x64 pixel resolution and is able to capture 1,400 frames per second. This camera is useful for recording solidification velocities less than 4 m/s. For intermediate and high undercoolings, a high-speed data acquisition system¹⁷ (HSDA96) is used. The HSDA96 is an 8-bit system featuring a 10x10 array of parallel-tapped photodiodes capable of capturing thermal images at 1 million frames per second. The experimental error associated with determining solidification velocity using thermal imaging techniques is $\pm 10\%$ ¹⁴. Thermal images captured using the Dalsa camera and HSDA96 are shown in figure 7.

While a large number of experiments on numerous alloys have been conducted at Vanderbilt, only the results of the following alloys are reported here: Ni-C, $k_E=0.1-0.2$; Ti-Ni, $k_E=0.2-0.3$; Ni-Sn, $k_E=0.3-0.5$; Ni-Cu, $k_E=0.6-0.7$; and Ni-Ti, $k_E=0.8-0.9$. These alloys were selected to represent a wide range of equilibrium partition coefficients.

Experimental Results

The solidification velocity measurements as a function of undercooling for the alloys are shown in figures 8 through 12. All alloys exhibit two plateaus with the exception of Ti-1^a/₀Ni in figure 9a (which only exhibits one plateau). The first plateau occurs at intermediate undercoolings, while the second plateau occurs at high undercoolings. It should be noted that no plateau at intermediate undercoolings appears in the results for the pure elements (figures 2-5) and, therefore, this intermediate plateau is a direct result of solute addition.

Altgilbers¹⁸ analyzed the microstructures of the processed samples as a function of undercooling and concluded that the first plateau is accompanied by a change in solidification morphology. Solidification morphology is dendritic for undercoolings less than that of the first plateau, while at higher undercoolings the morphology is cellular. In the second plateau, there is no distinguishable change in morphology and the structure remains cellular. The surface micrographs of Ni-10^a/₀Ti are shown in figure 13 as an example.

Altgilbers¹⁸ also conducted a microprobe analysis on Ni-10^a/₀Ti; the results are shown in figure 14. Figure 14 shows the nature of the decrease in the concentration difference across the dendrite tips as undercooling increases. The large decrease in concentration difference occurs at intermediate undercoolings in the range of the first plateau in Ni-10^a/₀Ti and is therefore indicative of the onset of solute trapping.

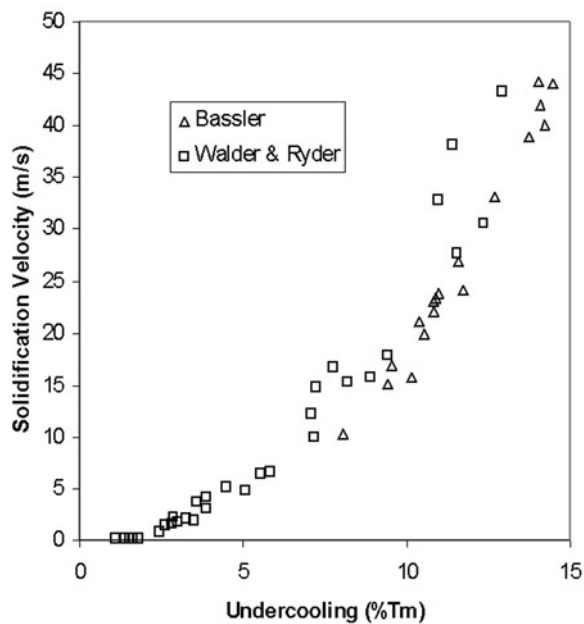


Figure 3: Solidification velocity of pure titanium as measured by Bassler¹⁴ and Walder and Ryder¹².

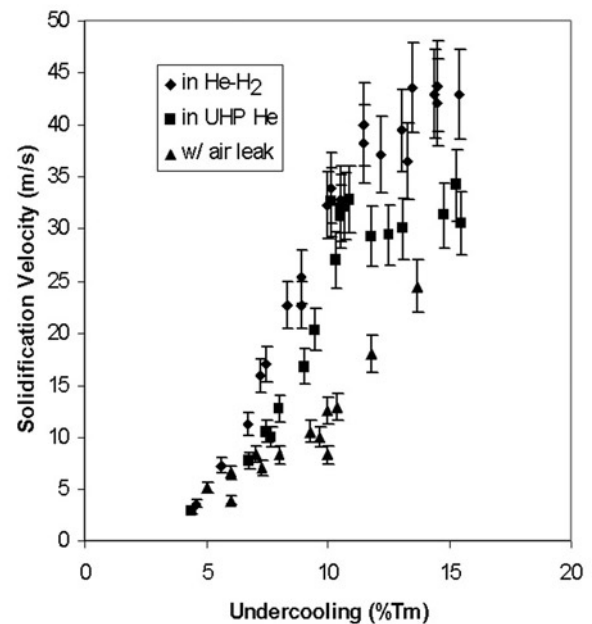


Figure 4: Solidification velocity of pure nickel in three different processing environments as measured by Bassler¹⁴.

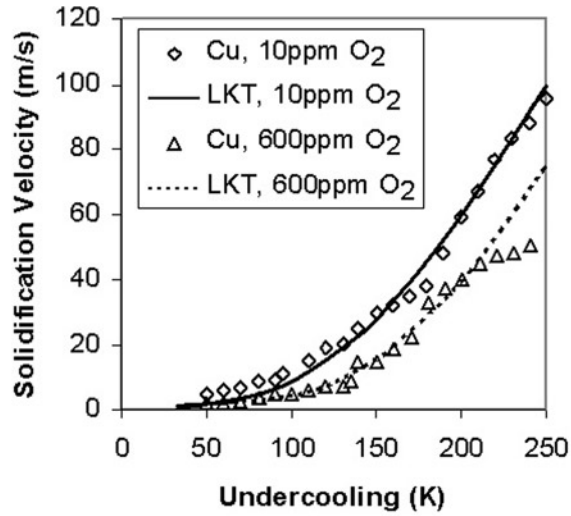


Figure 5: Solidification velocity of pure copper with two different oxygen concentrations by Cochrane et al¹⁵.

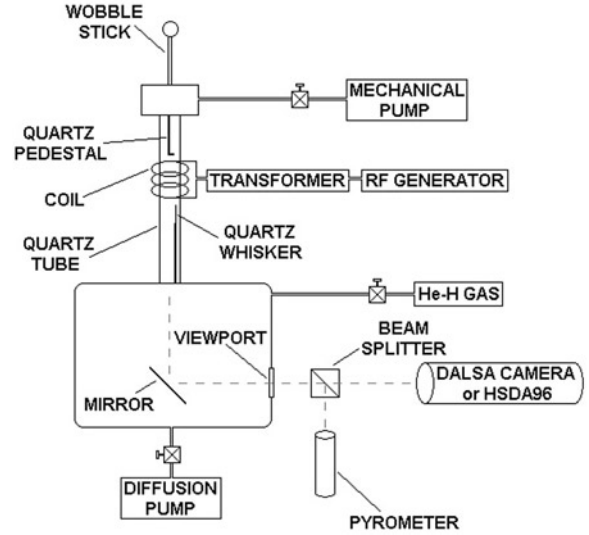


Figure 6: Schematic diagram of Vanderbilt's electromagnetic levitator.

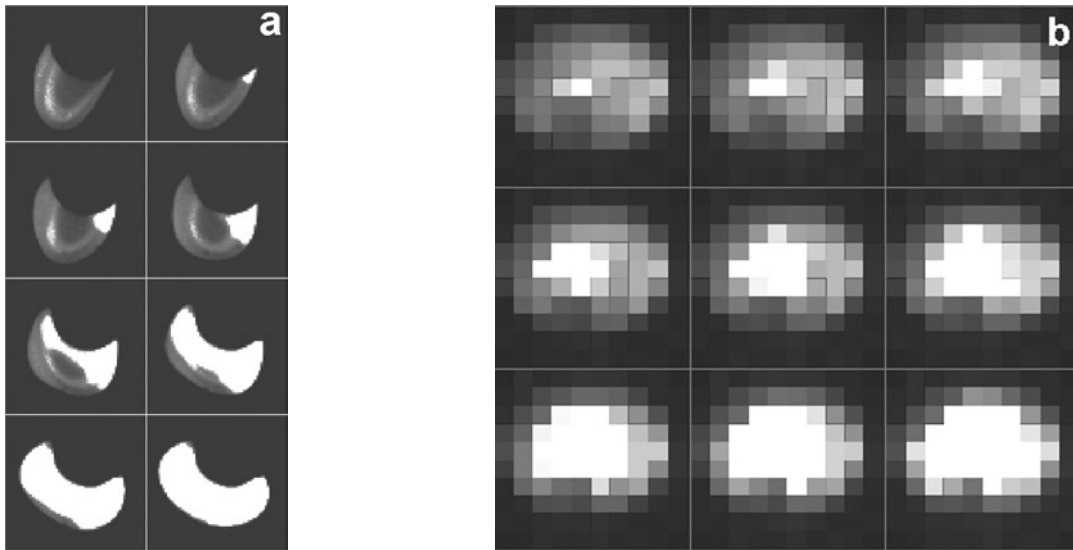


Figure 7: Thermal images of solidification taken with (a) Dalsa camera, Ni-based sample, 1.4ms per frame, solidification velocity = 0.6m/s and (b) HSDA96, Ti-based sample, 40μs per frame, solidification velocity = 16m/s. Bright areas represent solid, and dark areas represent undercooled liquid.

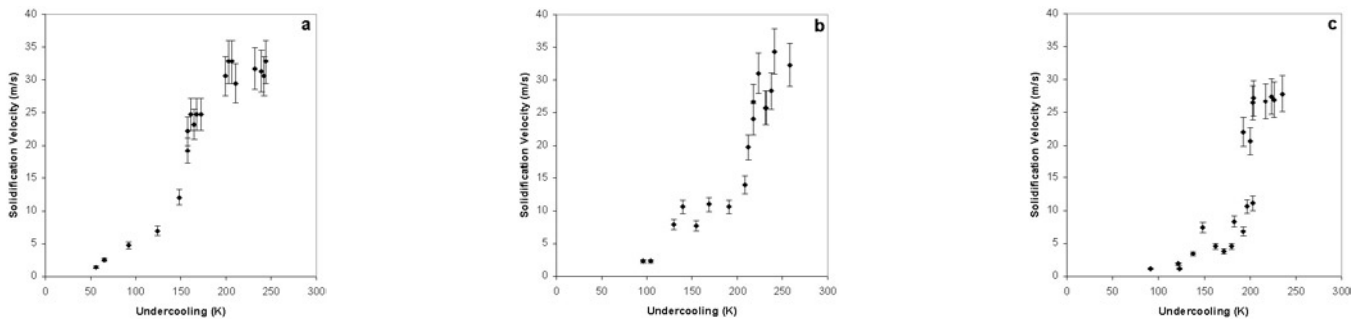


Figure 8: Solidification velocity of (a) Ni-0.6^a%C, (b) Ni-1.7^a%C and (c) Ni-2.8^a%C.

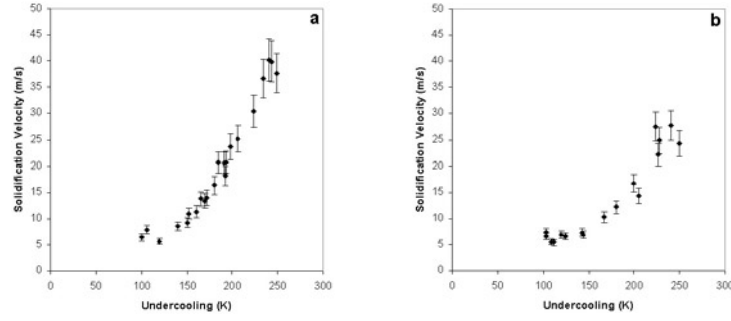


Figure 9: Solidification velocity of (a) Ti-1^a/₀Ni and (b) Ti-2^a/₀Ni.

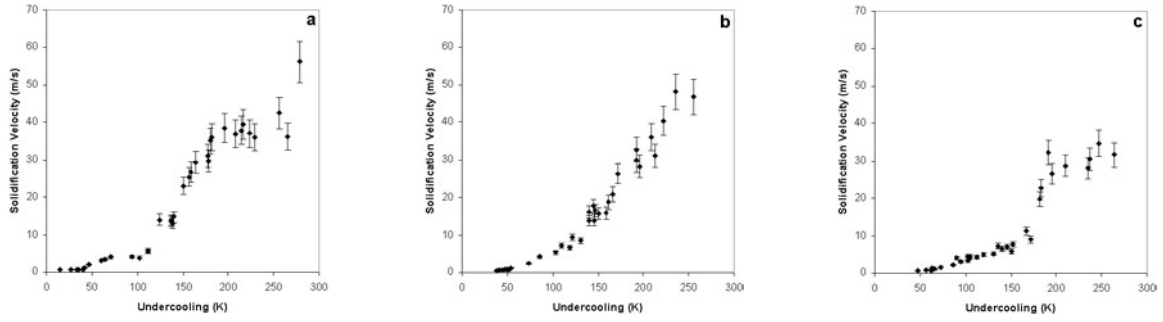


Figure 10: Solidification velocity of (a) Ni-1^a/₀Sn, (b) Ni-2.5^a/₀Sn and (c) Ni-4^a/₀Sn.

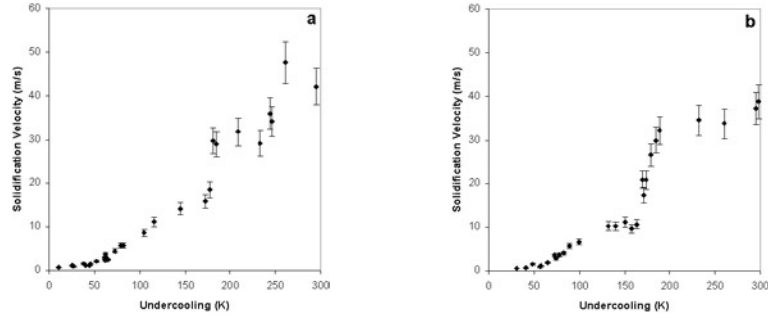


Figure 11: Solidification velocity of (a) Ni-5^a/₀Cu and (b) Ni-10^a/₀Cu.

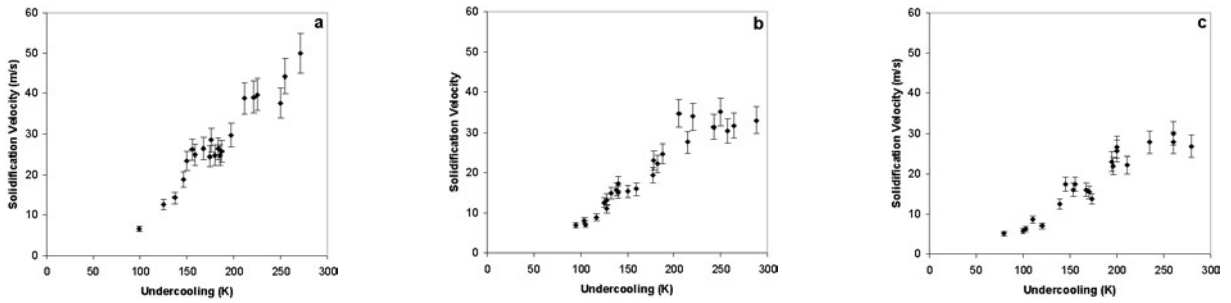


Figure 12: Solidification velocity of (a) Ni-3^a/₀Ti, (b) Ni-5^a/₀Ti and (c) Ni-10^a/₀Ti.

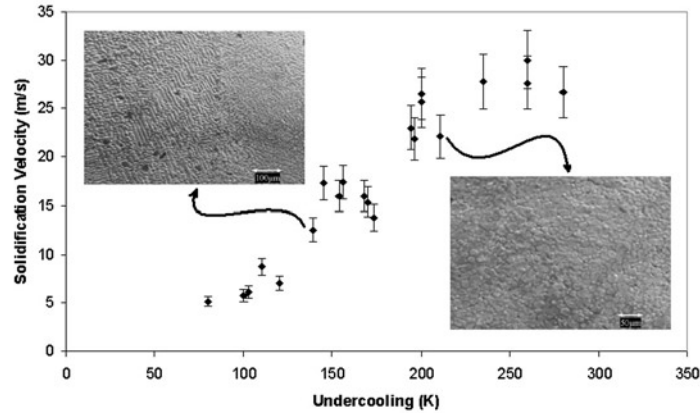


Figure 13: Microstructures of Ni-10_{a/o}Ti samples. At velocities below the first plateau, the solidification morphology is dendritic, while at higher velocities the morphology is cellular.

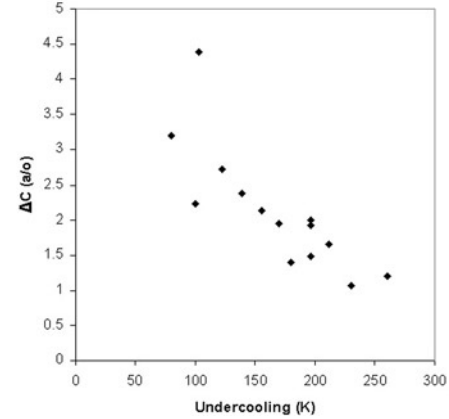


Figure 14: Microprobe analysis of Ni-10_{a/o}Ti samples showing a decrease in concentration difference across the dendrite tips with increasing undercooling.

Based on the results of residual oxygen's effects on the solidification velocity of pure elements at high undercoolings, it is hypothesized that the second plateau in the results for the alloys is also due to residual oxygen in the alloy system. Further investigation of solidification velocity while varying oxygen concentrations in alloys is required since interaction between solutes and oxygen may play a role in solidification behavior.

Application of IMS Modeling

The IMS model was applied to the results to test the agreement between theory and experiment. As examples, one of each of the results of the smallest k_E alloy (Ni-C) and largest k_E alloy (Ni-Ti) are plotted along with the IMS model in figures 15 and 16 respectively. Figures 15 and 16 show similar results. For both low k_E and high k_E examples, good agreement can only be attained by using a k_E in the calculations that is much smaller than the actual k_E . The parameters used for calculation of the solidification velocity versus undercooling curve for figures 15 and 16 are shown in table 2.

Conclusions

Solidification velocity decreases with increasing amounts of residual oxygen in otherwise pure nickel for all ranges of undercooling. Depending on the oxygen concentration, a solidification velocity plateau may appear in higher undercoolings.

In most alloys, there are two plateaus in the solidification velocity versus undercooling plot. The first plateau occurs in intermediate undercoolings and is a direct result of solute addition. Solute trapping and a change in solidification morphology from dendritic to cellular accompany the plateau. Based on the results for pure nickel, the second plateau in high undercoolings is hypothesized to be a result of residual oxygen in the alloy system. Further work is needed to quantify the oxygen concentration in alloys and relate the effect of oxygen to solidification velocity at high undercoolings.

The first solidification velocity plateau always occurs for alloys in intermediate undercoolings regardless of k_E . The IMS model does not predict a plateau in solidification velocity for high k_E alloys.

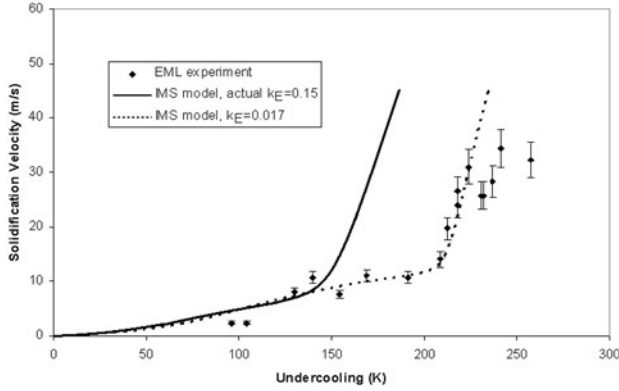


Figure 15: IMS modeling applied to Ni-1.7^a/₀C with actual k_E and calculational k_E used for fitting data.

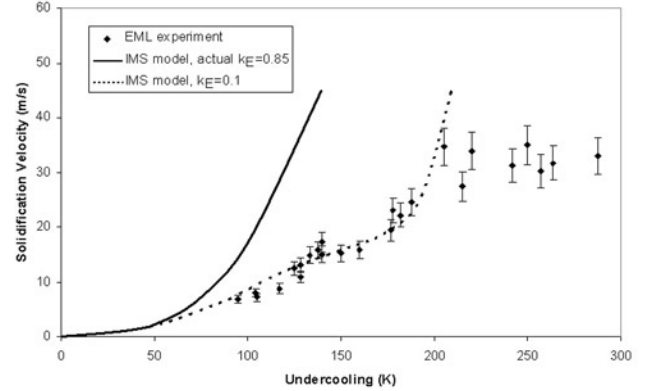


Figure 16: IMS modeling applied to Ni-5^a/₀Ti with actual k_E and calculational k_E used for fitting data.

Table 2: Parameters used in applying IMS model to Ni-1.7^a/₀C and Ni-5^a/₀Ti in figures 15 and 16 respectively.

	Ni-1.7 ^a / ₀ C, figure 15	Ni-5 ^a / ₀ Ti, figure 16
T_m (K)	1726	1726
L (J/mol)	17120	17120
C (J/molK)	43	43
a_o (m)	4×10^{-10}	4×10^{-10}
m_L (K/at%)	-14	-6
C_o (at%)	1.7	5
α (m ² /s)	6×10^{-6}	10^{-5}
D (m ² /s)	2.8×10^{-8}	6×10^{-8}
V_o (m/s)	4036	4036
σ (J/m ²)	0.21	0.23

The IMS model conforms to experiment for dilute alloys if the equivocal parameters are adjusted to fit experimental data and a calculational k_E is chosen that is less than the actual k_E of the alloy.

Finally, more theoretical and experimental work is needed in ternary systems and large k_E alloys in order to develop a model that fits experimental results.

Acknowledgements

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FREE DENDRITIC GROWTH OF SUCCINONITRILE-ACETONE ALLOYS WITH THERMOSOLUTAL MELT CONVECTION

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Abstract

A stagnant film model of the effects of thermosolutal convection on free dendritic growth of alloys is developed, and its predictions are compared to available earth-based experimental data for succinonitrile-acetone alloys. It is found that the convection model gives excellent agreement with the measured dendrite tip velocities and radii for low solute concentrations. However, at higher solute concentrations the present predictions show some deviations from the measured data, and the measured (thermal) Peclet numbers tend to fall even below the predictions from diffusion theory. Furthermore, the measured selection parameter σ^* is significantly above the expected value of 0.02 and exhibits strong scatter. It is shown that convection is not responsible for these discrepancies. Some of the deviations between the predicted and measured data at higher supercoolings could be caused by measurement difficulties. The systematic disagreement in the selection parameter for higher solute concentrations and all supercoolings examined, indicates that the theory for the selection of the dendrite tip operating state in alloys may need to be reexamined.

1. Introduction

Equiaxed dendrites are a frequently observed growth mode in metal alloy castings. Unlike columnar growth that occurs in directional solidification into a positive temperature gradient, equiaxed growth occurs within a supercooled melt where the crystals grow in an unconstrained or “free” manner until they interact with neighboring crystals or container walls. In free dendritic growth, the latent heat of fusion and the solute are rejected into the liquid ahead of the solid-liquid interface and the temperature gradient in the liquid at the interface is negative.

Free dendritic growth in pure substances, where the driving force is purely thermal, has been studied extensively and is reasonably well understood for both diffusion and convection controlled cases¹⁻⁸. The presence of coupled heat and species transport significantly complicates the analysis of free dendritic growth in alloys. The velocity of the dendrite tip experiences a maximum at a small, but finite solute concentration. Solute additions destabilize the tip, resulting in a smaller tip radius and hence a larger tip velocity. On the other hand, the much lower diffusion rate of solute compared to heat slows down the growth. These two competing effects cause the velocity maximum at small solute concentrations. Theories that have been proposed for diffusion controlled free dendritic growth in alloys qualitatively predict the velocity maximum (see below for a review). However, on earth and at low supercoolings, buoyancy driven convection is known to significantly influence the tip velocities and the overall growth of a dendrite⁵. In alloys, such convection is driven by both thermal and solutal gradients in the melt. The effect of convection on the dendritic growth of alloys is not yet fully understood despite its importance in metal alloy casting.

Keywords: dendritic growth, alloys, succinonitrile, convection, flight

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In this paper, a simple model is presented to describe the influence of thermosolutal convection on free dendritic growth of alloys. The model is developed within the framework of the well-known Lipton, Glicksman and Kurz (LGK) formulation^{9, 10} for diffusion controlled growth at low Peclet numbers, with the thermosolutal convection effects incorporated through a stagnant film approximation^{11, 12}. The model was primarily developed to predict quantitatively the dendrite tip velocities and radii measured in the earth-based succinonitrile-acetone (SCN-ACE) experiments of Chopra et al.¹³. To the authors' best knowledge, these remain the only experiments where both the dendrite tip velocity and radius were measured over a sufficiently large range of supercoolings and alloy compositions, and under conditions where convection can be expected to be important. Other experimental studies on dendritic growth in alloys (see, for example, Refs.¹⁴⁻¹⁷) do not report both the tip velocity and radius. The SCN-ACE system is well suited for comparison with theories because of the availability of a large body of both microgravity (diffusion controlled) and terrestrial (convection controlled) experimental data in the limit of vanishing solute concentration (i.e., pure SCN)^{4, 5, 18}, and because all relevant thermophysical properties are known accurately. The data of Chopra et al.¹³ displays the velocity maximum at small solute concentrations and has often been used to assess dendritic growth theories (see, for example, the review by Trivedi and Kurz¹⁹). These comparisons show relatively large discrepancies between the predictions and the measurements, especially at higher solute concentrations. It is shown in this paper that the discrepancies can only partially be explained by the influence of convection in the experiments, and that additional study of the alloy dendritic growth problem may be needed.

The paper is structured as follows. In Section 2, current theories of free dendritic growth of alloys are summarized, while Section 3 reviews previous models for pure substances that take into account the effect of natural convection. The present model of thermosolutal convection in free dendritic growth of alloy dendrites is presented in Section 4. Model results are presented in Section 5 and are compared to experiments for both pure SCN and SCN-ACE alloys. The conclusions of the present study are summarized in Section 6.

2. Theories of Free Dendritic Growth of Alloys

Before developing a model that includes convection, it is necessary to briefly review available theories of diffusion controlled free growth of alloy dendrites into a supercooled melt. These basic theories are concerned with the prediction of the steady-state tip velocity, V , and radius, R , of a branchless needle crystal. Langer²⁰, Lipton, Glicksman, and Kurz (LGK)^{9, 10}, and Karma and Langer²¹ have proposed the first model of free growth into a supercooled alloy melt. These models all use marginal stability theory²² to determine the operating point of the tip through the introduction of a stability constant $\sigma^* \sim 1/(R^2V)$. Lipton, Kurz, and Trivedi (LKT)²³ and Boettinger, Coriell, and Trivedi (BCT)²⁴ generalized the LGK model and extended it to high growth rates. The LGK model (or LKT or BCT models for rapid growth) is now the most commonly used model for free dendritic growth from a supercooled alloy melt and is reviewed in greater detail next. In 1985, Karma and Kotliar²⁵ developed the first microscopic solvability theory (MST) for the alloy case based on a boundary layer approximation for the thermal and solutal diffusion fields. Ben Amar and Pelcé²⁶ generalized this theory to a fully non-local model for alloy dendrites at low supercoolings. The MST theory uses the same framework as the LGK theory, except that the selection parameter σ^* is a function of the surface energy anisotropy strength.

The dendrite tip velocity and radius can be predicted by first considering the thermal and solutal transport at the tip. Taking into account the capillary correction and neglecting the kinetic effect, the total imposed

supercooling is given by

$$\Delta T = \Delta T_T + \Delta T_C + \Delta T_R \quad (1)$$

where ΔT_T , ΔT_C and ΔT_R are the thermal, solutal, and capillary contributions to the supercooling, respectively. The dimensionless thermal and solutal supercoolings are defined, respectively, as

$$\Omega_T = \frac{T_t^* - T_0}{L_f / c_L} \quad \text{and} \quad \Omega_C = \frac{C_t^* - C_0}{C_t^* (1-k)} \quad (2)$$

where L_f is the latent heat of fusion, c_L is the liquid specific heat, k is the partition coefficient, T_0 and C_0 are the initial or far-field melt temperature and solute concentration, respectively, and T_t^* and C_t^* are the temperature and solute concentration in the liquid at the dendrite tip, respectively. Approximating the capillary correction using the Gibbs-Thomson relation, Eq. (1) can be rewritten as¹⁹

$$\Delta T = \left(\frac{L_f}{c_L} \right) \Omega_T + \frac{k \Delta T_0 \Omega_C}{1 - (1-k) \Omega_C} + \frac{2\Gamma}{R} \quad (3)$$

where Γ is the Gibbs-Thomson coefficient and $\Delta T_0 = mC_0 (1 - 1/k)$ is the equilibrium freezing temperature range, in which m is the liquidus slope. The capillary contribution in Eq. (3) is relatively small for the supercoolings considered here, but is included nevertheless for completeness. The dimensionless thermal and solutal supercoolings in Eq. (3) are obtained from appropriate solutions of the transport problem for the dendrite tip. In the LGK model for diffusion controlled growth, they are calculated from the Ivantsov solutions for steady heat and species diffusion around a paraboloid of revolution, which can be written in terms of the thermal ($Pe_T = VR/2\alpha$) and solutal ($Pe_C = VR/2D$) Peclet numbers as

$$\Omega_T = \text{Iv}(Pe_T) \quad \text{and} \quad \Omega_C = \text{Iv}(Pe_C) \quad (4)$$

where Iv is the Ivantsov function¹⁹, D is the liquid mass diffusivity, and α is the liquid thermal diffusivity. According to the above equations, if the capillary correction can be neglected, the total supercooling is a function of the thermal and solutal Peclet numbers only. In the presence of convection, equations (4) are obviously not valid.

Introducing the stability constant or selection parameter σ^* , a second equation for the unknown dendrite tip velocity and radius is obtained. As shown by Trivedi and Kurz^{19, 27, 28}, for an isothermal solid with no solute diffusion in the solid, this equation can be written in the following general form

$$R = \left[\frac{\Gamma}{\sigma^* (mG_C - G_T/2)} \right]^{1/2} \quad (5)$$

where the thermal, G_T , and solutal, G_C , gradients are given by the following general flux balances at the interface

$$G_T = -(V/\alpha)L_f/c_L \quad (6)$$

$$G_C = -(V/D)C_t^*(1-k) \quad (7)$$

Corrections in Eq. (5) for large Peclet numbers¹⁹ are not needed for the small supercoolings considered here. Substituting Eqs. (6) and (7) into Eq. (5), the following tip radius selection criterion for free dendritic growth of alloys is obtained

$$R = \frac{d_0}{\sigma^* \left[2Pe_C \left(\frac{k \Delta T_0 / (L_f / c_L)}{1 - (1-k) \Omega_C} \right) + Pe_T \right]} \quad (8)$$

where $d_0 = \Gamma/(L_f/c_L)$ is the capillary length. According to Trivedi and Kurz¹⁹, σ^* as defined above is constant for a given alloy system (implying a fixed anisotropy strength) and independent of the Peclet numbers and solute concentration. Evidence indicates that for the experiments considered here, σ^* is also independent of the convection velocities in the melt. This issue is examined in greater detail below. In the LGK model for diffusion-controlled growth, Ω_c in Eq. (8) is calculated from the Ivantsov solution given by Eq. (4), $\Omega_c = \text{Iv}(\text{Pe}_c)$. As mentioned above, a different relation for Ω_c must be used in the presence of convection.

3. Models of Free Dendritic Growth of Pure Substances in The Presence of Natural Convection

The effects of melt flow on free dendritic growth of pure substances have been investigated both experimentally and analytically for almost three decades. Lee et al.⁵ present a comprehensive review of the literature on this subject. While most studies focus only on how heat transport away from the tip is modified by flow, Bouissou and Pelce²⁹ have extended the linearized solvability theory, which assumes a parabolic tip shape, to make quantitative predictions of the effect of a forced flow on the tip selection, i.e., on σ^* . They found that when the external flow velocity is small, the selection parameter σ^* is independent of the flow, but after a critical threshold value of the flow velocity the inverse of the selection parameter $1/\sigma^*$ increases almost linearly with the external flow velocity.

The theories that have been developed to predict the heat transport away from the tip in the presence of convection all reduce to the Ivantsov solution, Eq. (4), in the limit of no flow⁵. Ananth and Gill⁸ and Canright and Davis³⁰ derived exact solutions for various limiting cases involving thermally driven natural convection. These solutions are relatively complex and would be difficult to extend to thermosolutal convection in the case of alloys. A more simple approach is afforded by the use of so-called stagnant film models. Cantor and Vogel¹¹ derived a modified Ivantsov solution where the far-field supercooling condition is not applied at infinity, but at a confocal paraboloid located at a distance δ_T from the dendrite tip, as

$$\Omega_T = \text{Pe}_T \exp(\text{Pe}_T) \{E_1(\text{Pe}_T) - E_1[\text{Pe}_T(1 + 2\delta_T/R)]\} \quad (9)$$

where E_1 is the exponential integral function. For $\delta_T/R \rightarrow \infty$, the above equation reduces to the Ivantsov solution. The effects of convection on the growth are incorporated into the stagnant film model by evaluating the thickness of the thermal boundary layer, δ_T . This can be accomplished by choosing a suitable Nusselt number, Nu , correlation for the convective heat transfer at the dendrite tip and realizing that $\delta_T \sim \ell/\text{Nu}_\ell$, where ℓ is a characteristic length scale for convection. Then, the ratio δ_T/R needed in Eq. (9) is given by

$$\delta_T/R \sim (\ell/R)/\text{Nu}_\ell \quad (10)$$

Cantor and Vogel¹¹ used the dendrite tip radius as the characteristic length scale for convection, i.e. $\ell = R$, so that $\delta_T/R \sim 1/\text{Nu}_R$. This implies that a larger or global length scale, such as the size of the entire crystal or the size of the system in which the growth takes place, does not influence the convective heat transfer and, hence, the growth.

Sekerka et al.¹² used the stagnant film model to investigate the effect of orientation of a dendritic crystal relative to gravity on its growth in the presence of thermal natural convection. The characteristic length scale was chosen to be the length, L , of the dendrite arm, i.e. $\ell = L$, implying that the convection is driven by the overall size of the crystal. The Nusselt number was evaluated from a correlation for free convection

from a sphere of radius L , i.e. $Nu_L \sim Ra_L^{1/4}$, where Ra is the Rayleigh number. Since $Ra_L \sim L^3$, Eq. (10) can be rewritten in terms of a Rayleigh number based on the tip radius R as $\delta_T/R \sim (L/R)^{1/4}(Ra_R)^{-1/4}$. Hence, in Sekerka et al.'s model the thermal boundary layer thickness increases with $L^{1/4}$, or in other words, the heat transfer rate at the dendrite tip *decreases* with $L^{-1/4}$. This would result in a decrease in the tip velocity as the dendrite continues to increase in size, something that has not been observed experimentally. Typically, one would expect an opposite behavior where the natural convection becomes stronger as the crystal increases in size. Sekerka et al. set the length L to a constant of the order of several millimeters and did not investigate variations in the tip velocity. It should be noted also that Sekerka et al. took the same value for σ^* in diffusion dominated (microgravity) and convection (terrestrial) cases. They obtained good agreement with the pure SCN data from the earth-based experiments of Huang and Glicksman³¹.

Based on the results of two-dimensional phase-field simulations, Tonhardt and Amberg³² recently proposed a Nusselt number correlation for a downward growing dendrite tip in the presence of thermal convection. This correlation is based on the concept that the dendrite tip is a small object in a forced flow that is driven by the natural convection on the scale of the entire crystal. Hence, the Nusselt number at the tip is evaluated using a correlation for forced convection from an object of characteristic size R , i.e. $Nu_R \sim Pr^{0.4} Re_R^{1/2}$, where $Re_R = UR/\nu$ is the Reynolds number based on the tip radius, ν is the kinematic viscosity, and Pr is the Prandtl number. The velocity U is obtained by assuming that the flow is driven by natural convection on the scale of the entire crystal and by using the thermal convection analogy $Re_L \sim Gr_L^{1/2}$, where both the Reynolds and Grashof numbers (Gr) are based on the dendrite arm length L . This concept leads to $\delta_T/R \sim (R/L)^{1/4}(Ra_R)^{-1/4}$, implying that the heat transfer rate at the tip *increases* with $L^{1/4}$. This behavior is opposite to that predicted by Sekerka et al.'s model and appears to be more realistic. However, Tonhardt and Amberg's phase-field simulation results show that the tip heat transfer rate varies only with $L^{1/8}$. This reflects an even weaker dependence on the crystal size and results in only a minor increase of the tip velocity during growth³². Again, no experimental evidence is available to support any variation with L .

Schrage³³ also developed a simplified analytical model of dendritic growth of a pure substance under the influence of natural convection. The natural convection is treated as a tip-local process and is simplified by using a control volume technique. Technically, this model is similar to the stagnant film approach. It also gives good agreement with available experimental data for pure SCN.

4. Model of Free Dendritic Growth of Alloys in the Presence of Thermosolutal Convection

The present model of free dendritic growth of alloys in the presence of thermosolutal convection is based on the LGK model reviewed in Section 2 and the stagnant film modified Ivantsov solution for incorporating the effect of convection, as reviewed in Section 3. The choice of σ^* in the presence of convection is discussed in the next section. In the case of alloys, both thermal (δ_T) and solutal (δ_C) boundary layer thicknesses must be introduced to account for the thermosolutal convection effects in the stagnant film model. Thus, the Ivantsov solutions given in Eq. (4) are replaced by

$$\Omega_T = Pe_T \exp(Pe_T) \{E_1(Pe_T) - E_1[Pe_T(1 + 2\delta_T/R)]\} \quad (11)$$

$$\Omega_C = Pe_C \exp(Pe_C) \{E_1(Pe_C) - E_1[Pe_C(1 + 2\delta_C/R)]\} \quad (12)$$

The boundary layer thicknesses are estimated from appropriate Nusselt (Nu) and Sherwood (Sh) number correlations as

$$\delta_T/\ell = B/\text{Nu}_\ell \quad \text{and} \quad \delta_C/\ell = B/\text{Sh}_\ell \quad (13)$$

where ℓ is again a characteristic length scale for convection and B is a constant of proportionality.

Note that the same constant B is used in Eq. (13) for both boundary layer thicknesses. This is supported by the results of previous studies reviewed in Gebhart et al.³⁴, which show that a constant value of $B \approx 2$ is appropriate for both the thermal and solutal boundary layer thicknesses. This value is valid for the following ranges of the governing dimensionless parameters: $\text{Pr}=0.7$ to 7.0 , $\text{Sc}=0.94$ to 100 , and $N=0.5$ to 2 , where Sc is the Schmidt number and N is the buoyancy ratio. The buoyancy ratio is defined as $N = \beta_c \Delta C / (\beta_T \Delta T)$, where β_T and β_c are the thermal and solutal expansion coefficients, respectively, and ΔT and ΔC are characteristic temperature and concentration differences, respectively. A positive value for N implies that the thermal and solutal buoyancy effects assist each other. It can be verified that the SCN-ACE experiments considered here fall within the above ranges of the dimensionless parameters (see Table 1 and the results presented in the next section). An exact value for B is difficult to specify because of the ambiguity in defining the edge of the boundary layers. However, B is not equal to unity. The final choice for B is discussed below.

Gebhart et al.³⁴ examined numerous previous studies of external thermosolutal natural convection from a variety of geometries. They found that available Nusselt and Sherwood number correlations for $N > 0$ (assisting flows) can be written in the following general form

$$\text{Nu}_\ell = A (\text{Ra}_{\ell,T})^{1/4} \left(1 + \frac{N}{\sqrt{\text{Le}}} \right)^{1/4} \quad (14)$$

$$\text{Sh}_\ell = A (\text{Ra}_{\ell,C})^{1/4} \left(1 + \frac{\sqrt{\text{Le}}}{N} \right)^{1/4} \quad (15)$$

where A is a constant independent of Le and N. The Lewis number is defined as $\text{Le} = \text{Sc}/\text{Pr} = \alpha/D$. In the present application to dendritic growth, the thermal and solutal Rayleigh numbers are given, respectively, by

$$\text{Ra}_{\ell,T} = \frac{\beta_T g (T_t^* - T_0) \ell^3}{\alpha \nu} \quad \text{and} \quad \text{Ra}_{\ell,C} = \frac{\beta_C g (C_t^* - C_0) \ell^3}{D \nu} \quad (16)$$

and the buoyancy parameter is given by

$$N = \frac{\beta_C (C_t^* - C_0)}{\beta_T (T_t^* - T_0)} \quad (17)$$

In view of Eqs. (13) to (17), the ratio of the thermal to solutal boundary layer thicknesses is given by $\delta_T/\delta_C = \text{Sh}_\ell/\text{Nu}_\ell = \text{Le}^{3/8}$. Using the properties for SCN-ACE alloys provided in Table 1, it can be seen that the thermal boundary layer is approximately five times thicker than the solutal boundary layer. It is emphasized that the above correlations are not valid for alloys where the buoyancy ratio N is negative (such as Al-Cu)^{35, 36} and for liquid metals ($\text{Pr} \ll 1$). The convection correlations given by Eqs. (14) and (15) do not include the diffusion limit for vanishing Rayleigh numbers. This is done so that after substitution of the correlations into the stagnant film model, the Ivantsov solution is obtained as the diffusion limit.

The correlations given by Eqs. (14) and (15) have been found to be applicable to both vertical plates and spheres³⁴. Different geometries simply result in different values for the constant A. For example, the experiments of Mathers et al.³⁵ showed that for spheres $A=0.5$, if the sphere diameter d is chosen as the characteristic length. In the limit of purely thermal convection ($N=0$), Eq. (14) becomes $Nu_\ell = A(Ra_\ell)^{1/4}$. Hence, the value of the constant A may also be estimated from the extensive data and analyses available for purely thermal convection from various geometries. Acrivos³⁷ developed a boundary layer analysis for laminar natural convection that can be used to find the Nusselt number for any surface of revolution about an axis of symmetry. As part of the present study, this method was applied to a paraboloid of revolution pointing downward. It was found that $A \approx 0.9$ for the local Nusselt number at the stagnation point (with $\ell = R$). Since there is presently some uncertainty in the value for A for a dendrite, this issue is examined further below by comparing the predictions of the present model to experimental data for dendritic growth. Nonetheless, based on the analysis for a paraboloid of revolution, a value of $A \approx 0.9$ appears to be most appropriate for a downward growing dendrite tip.

The review of the previous convection models for dendritic growth of a pure substance in Section 3 and the discussion of Nusselt number correlations given above indicate that the tip radius R is an adequate characteristic length scale for natural convection from a downward growing dendrite tip. Furthermore, Chopra et al.¹³ do not report any temporal variations in the tip velocity in their SCN-ACE experiments, which implies no dependence on the dendrite arm length and provides only steady values of the tip radius and velocity. Using $\ell = R$, Eqs. (14) and (15) can be combined with Eq. (13) to give the following final expressions for the thermal and solutal boundary layer thicknesses for use in the stagnant film model

$$\frac{\delta_T}{R} = \frac{B}{A} (Ra_{R,T})^{-1/4} \left(1 + \frac{N}{\sqrt{Le}} \right)^{-1/4} \quad (18)$$

$$\frac{\delta_C}{R} = \frac{B}{A} (Ra_{R,C})^{-1/4} \left(1 + \frac{\sqrt{Le}}{N} \right)^{-1/4} \quad (19)$$

Note that only the ratio B/A appears in the above expressions. Based on the previous discussion, the estimated value of this ratio for a downward growing dendrite tip is $B/A \approx 2.2$. However, due to the uncertainties in both A and B, a more definite value of the ratio is determined in the next section by comparing the predictions of the present model with earth-based dendritic growth experiments for pure SCN. Here, it should be kept in mind that the ratio B/A can vary with the orientation of the dendrite with respect to gravity¹².

5. Results and Discussion

5.1. Model calibration for pure SCN

The ratio B/A in the expressions for the boundary layer thicknesses, Eqs. (18) and (19), is determined using the free dendritic growth data for pure SCN listed in Koss et al.¹⁸. This can be accomplished by comparing measured and predicted Peclet numbers as a function of the imposed supercooling. The present model equations readily reduce to the limiting case of a pure substance by setting the alloy concentration to zero. Equation (18) for the thermal boundary layer thickness reduces to $\delta_T/R = (B/A)Ra_{R,T}^{-1/4}$. When convection is absent, $Ra_{R,T} \rightarrow 0$ and $\delta_T/R \rightarrow \infty$. Then, according to Eq. (11), Pe_T is a function of the thermal supercooling, Ω_T , only. However, when predicting Pe_T as a function of the total supercooling, ΔT , Pe_T also depends on σ^* , because the capillary supercooling is a function of the tip radius R [see Eq. (3)]. According to Eq. (8), σ^* is needed to calculate R . Fortunately, the capillary supercooling is relatively small for the ΔT considered here. In the presence of convection, the predicted Pe_T is a stronger function of σ^* , because the thermal boundary layer thickness, δ_T , depends on the tip radius R . Hence, even though the variation of

Table 1: Properties of Succinonitrile and Succinonitrile-Acetone Alloys

	Symbol	Property	Value	Ref.
SCN	T_m	Melting point	331.233 K	[18]
	α	Liquid thermal diffusivity	$1.134 \times 10^5 \mu\text{m}^2/\text{s}$	[18]
	Γ	Gibbs-Thomson coefficient	$6.525 \times 10^{-2} \text{ K}\mu\text{m}$	[18]
	L_f/c_L	Unit supercooling	23.13 K	[18]
	d_0	Capillary length	$2.821 \times 10^{-3} \mu\text{m}$	[18]
	Pr	Prandtl number	23.1	[6,8]
SCN-Acetone	D	Liquid mass diffusivity	$1.27 \times 10^3 \mu\text{m}^2/\text{s}$	[10]
	m	Liquidus slope	-2.16 K/mol%	[10]
	k	Equilibrium partition ratio	0.103 mol%/mol%	[10]
	β_T	Thermal expansion coefficient	$7.91 \times 10^{-4}/\text{K}$ at T_m	[38]
	β_c	Solutal expansion coefficient	$1.68 \times 10^{-3}/\text{mol\%}$ at T_m (converted from $2.32 \times 10^{-3}/\text{wt\%}$)	[38]

Pe_T with ΔT can be used to assess the transport part of dendritic growth theories, a σ^* dependence remains especially in the presence of convection.

An appropriate value for σ^* for pure SCN can be found from Eq. (8), which reduces for a pure substance to

$$\sigma^* = \frac{2d_0\alpha}{R^2V} \quad (20)$$

By substituting the measured dendrite tip radius and velocity data for *both* the microgravity and earth-based experiments listed in Ref.¹⁸ into the above equation, a value of $\sigma^*=0.02$ is found to reasonably well represent the data at all supercoolings. Hence, this measured value for σ^* is taken here to determine the ratio B/A.

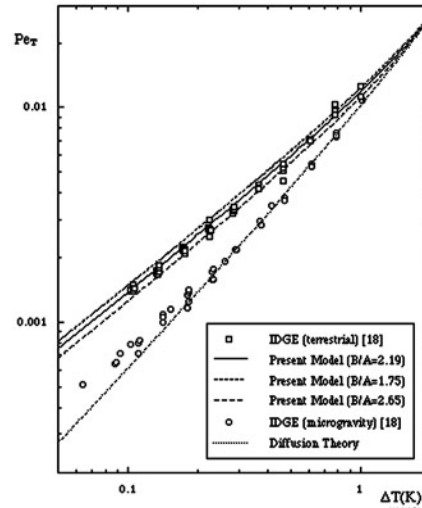


Figure 1. Comparison of measured and predicted tip Peclet numbers as a function of supercooling for pure SCN.

Figure 1 shows a comparison of the measured and predicted thermal Peclet numbers, $Pe_T = RV/2\alpha$, as a function of the total supercooling. As shown before, excellent agreement is obtained between the diffusion theory and the microgravity data, except for some disagreement at very low supercoolings due to a wall effect¹⁸. For the present convection model, three different lines are drawn in Figure. 1, corresponding to $B/A=1.75$, 2.19, and 2.65 (i.e., $2.19 \pm 20\%$). The line for $B/A=2.19$ represents the best fit of the present model to the terrestrial data, and good agreement is obtained over the entire supercooling range. The lines for $B/A=1.75$ and 2.65 nicely envelope the terrestrial data, indicating that the uncertainty in B/A is less than 20%.

The value $B/A=2.19$ found above is very close to the estimate made in the previous section from an analysis of the thermal convection boundary layer thickness at the stagnation point of a paraboloid of revolution growing downward into the melt (i.e., $B/A \approx 2.2$). This agreement lends considerable confidence to the present model, since the terrestrial data of Ref.¹⁸ can be assumed to correspond to downward growing dendrite tips. It also indicates that the choice of the convection length scale (R) is appropriate for pure SCN.

5.2. Model results for SCN-ACE alloys

Before comparing the present model for the effect of thermosolutal convection on free dendritic growth to the alloy experiments of Chopra et al.¹³, it is instructive to examine the variation of the various model parameters with solute concentration. For this purpose, calculations were performed using the properties of SCN-ACE alloys listed in Table 1, $B/A=2.19$, and $\sigma^* = 0.02$. As mentioned in Section 2, σ^* as defined in Eq. (8) should be independent of the solute concentration¹⁹. Thus, the σ^* value for pure SCN, as determined from both microgravity and terrestrial data (see Section 5.1), is used in this section. Note that the thermal and solutal expansion coefficients for SCN-ACE alloy melts listed in Table 1 have only recently been measured³⁸. The results of the model calculations are shown in Figure 2.

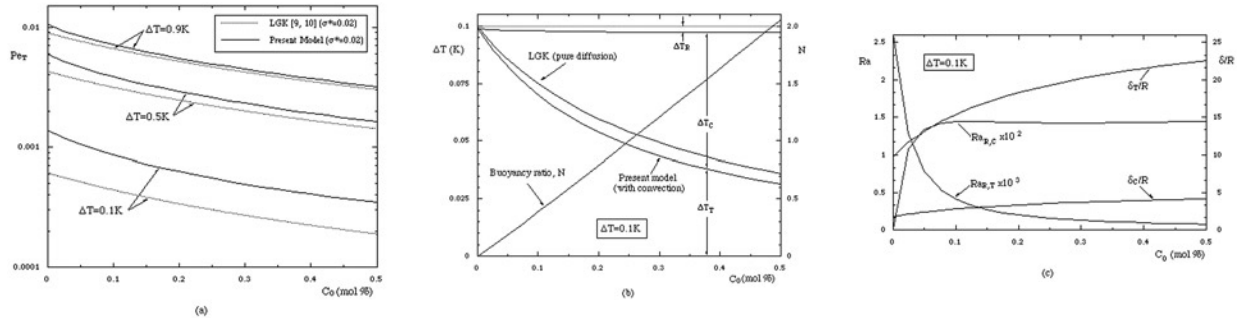


Figure 2. Model results for SCN-ACE alloys: (a) variation of predicted tip Peclet numbers with C_0 for three total supercoolings, (b) variation of predicted thermal, solutal, and capillary supercoolings and the buoyancy ratio with C_0 for $\Delta T=0.1$ K, and (c) variation of predicted Rayleigh numbers and boundary layer thicknesses with C_0 for $\Delta T=0.1$ K.

Figure 2a shows predicted thermal Peclet numbers, Pe_T , as a function of solute concentration for three different supercoolings ($\Delta T = 0.1$ K, 0.5 K, and 0.9 K) (note that the solutal Peclet number differs from Pe_T only by a constant factor equal to the Lewis number). Corresponding model predictions for diffusion controlled growth (labeled as “LGK”) are included in the figure for easy reference. At vanishing solute concentration ($C_0 = 0$), the Peclet numbers in Figure 2a correspond to those shown in Figure 1 for pure SCN. With increasing solute concentration, the predicted Peclet numbers decrease for both the convection and

the diffusion case. This can be explained by the much lower diffusion rate of solute compared to heat ($\alpha \gg D$), which tends to reduce the transport at the dendrite tip with increasing C_0 . The Peclet numbers predicted by the convection model are above those from the diffusion theory since in the present model convection always enhances the transport at the tip. As for pure SCN, the predicted convection effect is stronger at the lower supercoolings (0.1 K and 0.5 K) and relatively weak at 0.9 K. Although not readily apparent from the plot in Figure 2a (due to the log scale used; see also Figure 6 below), the Peclet numbers predicted by the convection model approach those from the diffusion theory for increasing solute concentration; i.e., the convection effect is weakening with increasing C_0 . As is shown below, this result can be explained by a drastic weakening of the thermal convection for increasing solute concentrations. However, it should not be generalized to solute concentrations greater than 0.5 mol% and alloys other than SCN-ACE.

Figure 2b shows the calculated variation of the thermal, solutal, and capillary supercoolings with solute concentration for a total supercooling of $\Delta T = 0.1$ K. With increasing solute concentration, the solutal supercooling increases at the expense of the thermal supercooling, while the capillary contribution remains very small as expected. Interestingly, the differences between the present convection model and the diffusion theory (LGK) are relatively minor, with the convection model giving slightly larger solutal supercoolings. This can be attributed to the fact that regardless of the transport, the three individual supercoolings must add up to the total supercooling (0.1 K in Figure 2b). The shift between the thermal and solutal contributions to the total supercooling due to convection is simply a reflection of the relative strengths of the thermal and solutal buoyancy forces changing with C_0 . Figure 2b shows that the ratio of the solutal to the thermal buoyancy forces, as described by the parameter N , increases almost linearly with C_0 . At the largest solute concentration shown (0.5 mol%), the buoyancy parameter is approximately equal to two.

Figure 2c shows the calculated variation of the Rayleigh numbers and boundary layer thicknesses with solute concentration for a total supercooling of $\Delta T = 0.1$ K. The thermal Rayleigh number, $Ra_{R,T}$, decreases sharply as soon as some solute (ACE) is added to the SCN. This can be attributed to the simultaneous decreases in the thermal supercooling (see Figure 2b) and the dendrite tip radius, R , (see Figure 3a below) with increasing C_0 . The decrease in $Ra_{R,T}$ becomes more gradual at solute concentrations greater than about 0.1 mol%. On the other hand, the solutal Rayleigh number, $Ra_{R,C}$, increases strongly for solute concentrations below 0.1 mol%, and then reaches an approximately constant value. This can be explained by the competition between the increasing solutal supercooling and the decreasing tip radius in $Ra_{R,C}$. Note that $Ra_{R,C}/Ra_{R,T} = NLe$. The continued decrease in $Ra_{R,T}$ coupled with the constancy in $Ra_{R,C}$ for $C_0 > 0.1$ mol% explains why the effect of convection on the predicted Peclet numbers (and, hence, the transport at the dendrite tip) diminishes with increasing solute concentration, as noted in connection with Figure 2a. Finally, Figure 2c shows that the dimensionless thermal, δ_T/R , and solutal, δ_C/R , boundary layer thicknesses both increase with increasing solute concentration. This also implies that the convection effect is weakening with increasing C_0 . It is interesting to note that the solutal boundary layer thickness ranges from one to five times the tip radius for $\Delta T = 0.1$ K. As noted earlier, $\delta_T/\delta_C = Le^{3/8} \approx 5.4$.

5.3. Comparison of the stagnant film model with SCN-ACE experiments of Chopra et al.

The present model of free dendritic growth in the presence of thermosolutal convection is compared with the earth-based experiments of Chopra et al.¹³ for SCN-ACE alloys. The dendrite tip velocity and radius data were extracted from the figures in Chopra et al. The estimated uncertainty in reading each individual datum is included in the following Figures (Figures 3 to 5). No uncertainties are shown for the data at 0.5 K, because these data could be read more accurately than the size of the symbols. Chopra et al. do not

discuss their experimental uncertainty. Also included in the following figures are some of the terrestrial data for pure SCN from Ref.¹⁸ already shown in Figure 1. The data from Chopra et al.¹³ for $C_0 = 0$ agree well with those from Ref.¹⁸, indicating that the procedure used for extracting the data from the figures in Chopra et al. is relatively accurate. The agreement for $C_0 = 0$ also implies that the data from Refs.^{13, 18} correspond to the same or similar orientations of the dendrite with respect to gravity (i.e., downward growth).

As a first step, the measured and predicted dendrite tip velocities and radii as a function of the solute concentration C_0 are compared for imposed total supercoolings, ΔT , of 0.1 K, 0.5 K and 0.9 K in Figures 3, 4 and 5, respectively. Corresponding model predictions for diffusion controlled growth (labeled as “LGK”) are included in the Figures for easy reference. In this comparison, $B/A=2.19$ and the σ^* value determined for pure SCN (i.e., $\sigma^*=0.02$) are used in the model calculations. As noted before, σ^* as defined in Eq. (8) should be independent of the solute concentration¹⁹. Furthermore, since the microgravity and terrestrial data for pure SCN in Ref.¹⁸ yield approximately the same σ^* at all supercoolings (see Section 5.1), it is reasonable to expect that σ^* is also independent of the convection intensity in the alloy experiments of Chopra et al.¹³. However, a more detailed examination of the effects of solute concentration and convection on σ^* is provided in Section 5.4.

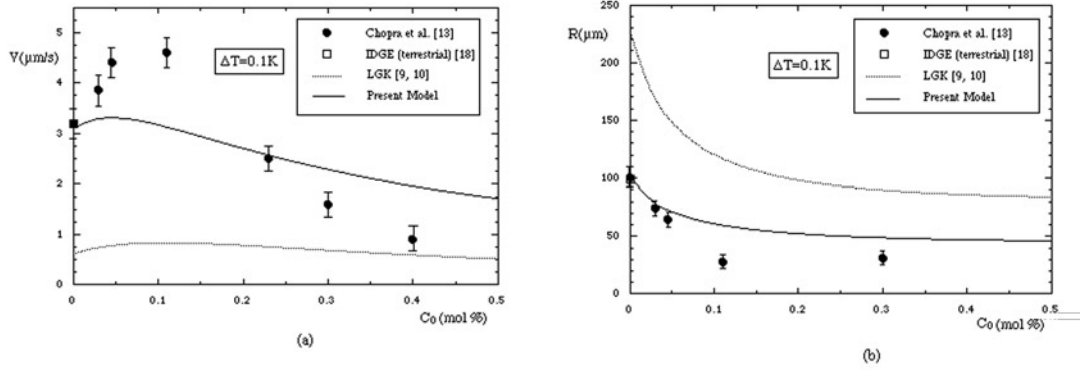


Figure 3. Comparison of measured and predicted dendrite tip growth velocities (a) and radii (b) as a function of solute concentration for SCN-ACE alloys at $\Delta T=0.1$ K.

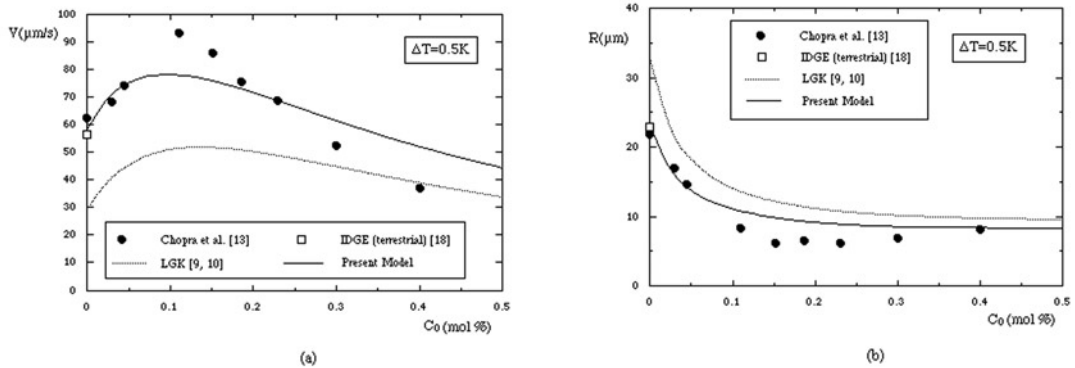


Figure 4. Comparison of measured and predicted dendrite tip growth velocities (a) and radii (b) as a function of solute concentration for SCN-ACE alloys at $\Delta T=0.5$ K.

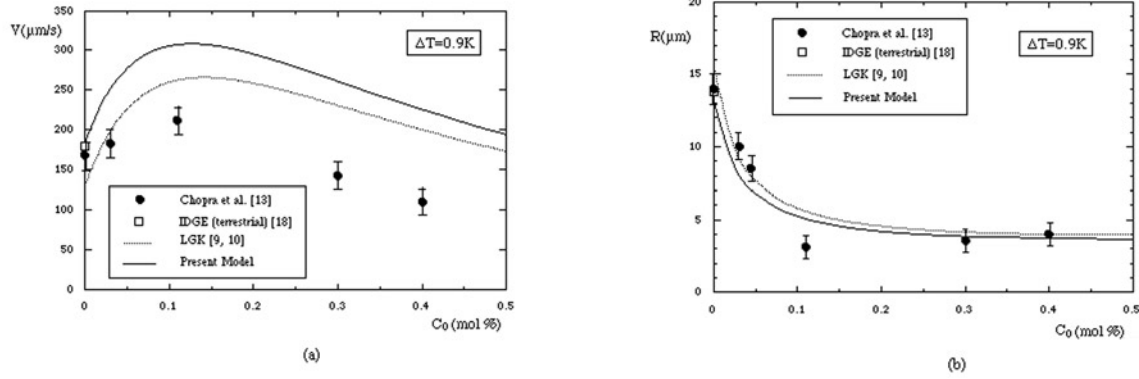


Figure 5. Comparison of measured and predicted dendrite tip growth velocities (a) and radii (b) as a function of solute concentration for SCN-ACE alloys at $\Delta T=0.9$ K.

It can be seen from Figures 3 to 5 that there is approximate, qualitative agreement between the predictions and measurements. Both the data and the model show an initial increase in the tip velocity with solute concentration, a maximum around 0.1 mol%, and a continual decrease at larger C_0 . On the other hand, the tip radii continually decrease with C_0 . As mentioned in the Introduction, the initial strong decrease in the tip radius is caused by destabilization of the tip by the solute, while the decrease in the tip velocity at larger C_0 is due to the fact the mass diffusivity is much smaller than the thermal diffusivity.

Figures 3 to 5 show that the convection effect is strongest at the lowest supercooling. For the 0.1 K supercooling (Figure 3), the maximum measured tip velocity is about four times higher than the prediction from diffusion theory. At the intermediate supercooling (0.5 K, Figure 4), the maximum tip velocity is still measured to be about twice the value predicted by the diffusion theory. For both the 0.1 K and 0.5 K supercoolings, the measured tip velocities approach the diffusion theory curve at higher solute concentrations, indicating that the convection effect diminishes as C_0 increases. At the highest supercooling (0.9 K, Figure 5), the present model indicates that the convection effect is small (see also Figure 2). Surprisingly, except for the datum at $C_0 = 0$, it can be seen from Figure 5a that the measured tip velocities are, as much as a factor of two, *below* the curve corresponding to purely diffusive growth. On the other hand, the measured tip radii at 0.9 K are relatively close to the predictions.

It is apparent from Figures 3 to 5 that the present convection model agrees better with the Chopra et al. data than the diffusion theory. As expected from Figure 1, the agreement is excellent at vanishing solute concentrations. Overall, the agreement between the measured and predicted tip radii (Figures 3b to 5b) is relatively good at all supercoolings and solute concentrations. However, at higher solute concentrations, large disagreements can be observed in Figures 3a to 5a between the measured and predicted tip velocities. For example, for a supercooling of 0.1 K (Figure 3a) when the convection effect is strongest, the measured maximum tip velocity (at around 0.1 mol%) is still 50% higher than predicted by the present model. At the largest solute concentration (0.4 mol%), the measured velocity is significantly below the prediction from the convection model. At 0.5 K (Figure 4), the agreement between the convection model and the measured data appears to be somewhat better, but again the measured tip velocities decrease much faster with increasing solute concentration than predicted. At a supercooling of 0.9 K (Figure 5), when the convection effect is least important, the measured velocities at higher solute concentrations are below even the predictions from diffusion theory, and thus the convection model only worsens their prediction.

To better understand the discrepancies between the present convection model and the measured tip velocities at all but the smallest solute concentrations, the measured and predicted thermal Peclet numbers, Pe_T , are compared in Figure 6 as a function of solute concentration. It can be seen that at lower solute concentrations (for $C_0 \leq 0.05$ mol%), the agreement between the measured and predicted Peclet numbers is good. At higher solute concentrations ($C_0 > 0.1$ mol%), however, the experimental Pe_T numbers fall consistently below the convection model predictions and at the two higher supercoolings (Figures 6b and 6c), they are even below the diffusion predictions.

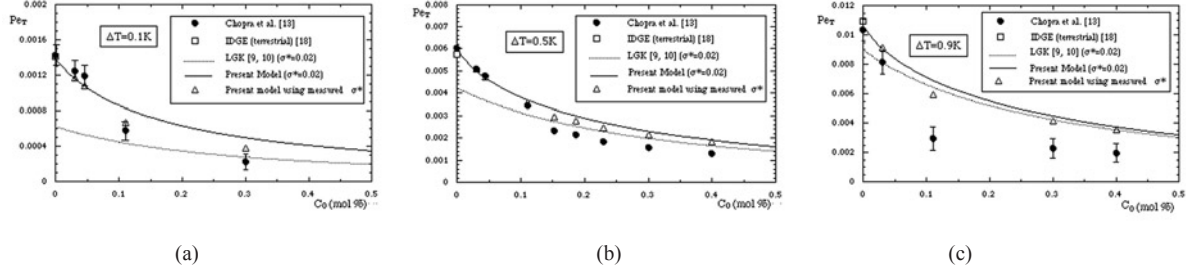


Figure 6. Comparison of measured and predicted thermal Peclet numbers as a function of solute concentration for SCN-ACE alloys at (a) $\Delta T=0.1$ K, (b) $\Delta T=0.5$ K, and (c) $\Delta T=0.9$ K.

One possible reason for this behavior could be that the thermosolutal convection *reduces* the heat transport at the tip, below the diffusion rate. This, in turn, would imply that the melt flows *downward* along the dendrite, in the same direction as the downward tip velocity, and advects heat/solute from the upstream portion of the dendritic crystal toward the tip. Hence, with increasing solute concentration, the flow would need to reverse direction from upward for pure SCN to downward for more concentrated SCN-ACE alloys. This behavior would be in contradiction with expectation and the present model. Since the buoyancy parameter N is positive in the present model (i.e., the heating of the melt by the dendrite and the rejection of ACE into the melt at the interface both decrease the melt density), the thermal and solutal buoyancy are aiding each other. The flow can be expected to be upward everywhere near the downward growing dendrite tip, because the large Pr and Sc numbers of the SCN-ACE system imply that the velocity boundary layer is thicker than the thermal and solutal boundary layers.

Another possibility is that the data of Chopra et al. do not correspond to downward growing dendrite tips, but to some other orientation of the dendrite with respect to gravity. For example, if a dendrite were growing upward, the flow would indeed be in the same direction as the tip velocity, resulting in a reduction in the heat/solute transport at the tip. Although Chopra et al. do not explicitly report the directions of the dendrite tip growth velocities with respect to gravity, there is strong evidence that all data correspond to approximately downward growing tips¹⁸. The good agreement between the measured and predicted Peclet numbers at low solute concentrations supports this conclusion. Hence, the orientation effect is unlikely to explain the disagreements in Figure 6 at higher solute concentrations.

It is especially puzzling that the largest deviations of the measured Pe_T from the model occur at a supercooling of 0.9 K (Figure 6c), where the convection effect on the growth is weakest. In other words, no matter what the direction of the flow is with respect to the dendrite, one would not expect at this supercooling that the measured Pe_T is different from the diffusion value by up to a factor of two.

The above discussion indicates that a different convection model is unlikely to reduce the disagreement between the measured and predicted thermal Peclet numbers at the larger supercoolings and larger solute concentrations. It points to a more fundamental problem with the theory or perhaps the experimental data. Although the dependence of the Peclet number on σ^* is weak at the larger supercoolings and larger solute concentrations, the use of $\sigma^*=0.02$ in the above comparisons also needs to be examined further.

5.4. Examination of the selection parameter σ^*

In view of the difficulties in reconciling the experiments and transport theories at higher solute concentrations, it is useful to also examine how the measurements of Chopra et al.¹³ agree with the selection criterion in the dendritic growth theory. The general selection criterion for alloys, as reviewed in Trivedi and Kurz¹⁹ and given by Eq. (8), can be solved for the selection parameter σ^* as

$$\sigma^* = \frac{d_0/R}{2Pe_C \frac{k \Delta T_0 / (L_f / c_L)}{1 - (1-k)\Omega_C} + Pe_T} \quad (21)$$

It is emphasized again that σ^* as defined above should be independent of the solute concentration C_0 and the imposed supercooling¹⁹. An experimental value for σ^* can, in principle, be obtained by substituting a measured pair of dendrite tip velocity and radius into Eq. (21) (note that $Pe \sim RV$). However, the presence of the solutal supercooling Ω_C in Eq. (21) renders σ^* dependent on the transport at the tip. Note that for pure substances $\Omega_C = 0$ and σ^* is independent of the transport. In the present determination of σ^* from experimental data, Ω_C must be calculated, since the solute concentration at the tip, C_t , is not known from measurements. Here, this is accomplished using either the Ivantsov solution given by Eq. (4) or the stagnant film modified Ivantsov solution given by Eq. (12), using measured V and R data.

Figure 7 shows the variation of the selection parameter σ^* calculated from the measured tip velocities and radii of Chopra et al. at three supercoolings as a function of the solute concentration C_0 . The uncertainty bars for σ^* propagate from the uncertainties in the V and R data. It can be seen that all σ^* obtained using the Ivantsov solution to calculate Ω_C (labeled as “LGK”) are within about 2% of the σ^* obtained using the stagnant film model for Ω_C (labeled as “Present Model”). The difference can be expected to be small, because the solutal supercooling is only weakly affected by convection (see Figure 2b). Thus, the σ^* plotted in Figure 7 are insensitive to the convection intensity in the transport solution used to calculate Ω_C ; however, this does not necessarily imply that σ^* is independent of the convection intensity.

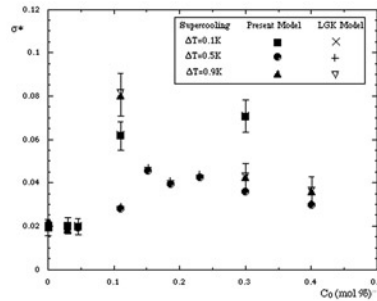


Figure 7. Selection parameter σ^* determined from Eq. (21) using the measured dendrite tip velocity and radius data for SCN-ACE alloys of Chopra et al.¹³. For the symbols labeled “Present Model,” the stagnant film model is used to determine Ω_C in Eq. (21); for the symbols labeled “LGK Model,” the Ivantsov model is used for Ω_C .

Figure 7 shows that for $C_0 \leq 0.05$ mol%, σ^* is indeed independent of the solute concentration. Furthermore, the value of 0.02 determined from the pure SCN microgravity and terrestrial data of Koss et al.¹⁸ is confirmed by the terrestrial Chopra et al. data for $C_0 \leq 0.05$ mol% and all three supercoolings. Since different supercoolings and solute concentrations imply different convection intensities, it can be said with certainty that σ^* is indeed independent of the convection intensity for $C_0 \leq 0.05$ mol%.

However, at higher solute concentrations ($C_0 > 0.1$ mol%) the experimentally determined σ^* in Figure 7 are much larger than 0.02 and can reach values as high as 0.08. There appears to be no pattern in the variation of σ^* with the solute concentration. Even if the largest values are ignored, the σ^* for $C_0 > 0.1$ mol% still average at least 0.04. Considering that only the Chopra et al. data appear to be available for direct testing of the free dendritic growth theory for alloys¹⁹, and that this theory has been used literally hundreds of times in a variety of alloy solidification models³⁹, the lack of agreement at higher solute concentrations is discouraging. Certainly, the scatter in the measured σ^* for $C_0 > 0.1$ mol% cannot be explained by any existing theory. As shown before, convection actually becomes weaker with increasing solute concentration; thus, convection is unlikely to be the reason for the scatter in σ^* for $C_0 > 0.1$ mol%. Furthermore, the convection intensity is primarily controlled by the imposed supercooling, and no consistent variation of the measured σ^* with ΔT can be discerned from Figure 7.

The issue of the dendrite tip operating state selection in SCN-ACE alloys can be viewed from a different perspective by using the following definition of the selection parameter¹⁹

$$\sigma_c^* = \frac{2\alpha d_0}{VR^2} \quad (22)$$

This alternative definition gives a selection parameter that continually varies with C_0 but is relatively independent of supercooling. Note that $\sigma_c^* = \sigma^*$ for $C_0 = 0$. An experimental value of σ_c^* can simply be obtained by substituting a measured pair of V and R into Eq. (22); thus, the uncertainty with respect to calculation of Ω_c in Eq. (21) is removed. A prediction of σ_c^* can be obtained by using the present model to calculate a pair of V and R and then substituting it into Eq. (22).

The measured and predicted σ_c^* are shown in Figure 8 as a function of C_0 for the three supercoolings. The differences between the predictions of the diffusion (labeled as “LGK”) and convection (labeled as “Present Model”) models are negligibly small, indicating that the convection effect on the calculated σ_c^* is small. As in the previous Figure the agreement between the experiments and theory is excellent for $C_0 \leq 0.05$ mol%. At higher solute concentrations, the measured σ_c^* values are substantially larger than the predictions. The disagreement appears to be of a systematic nature (as opposed to the scatter in σ^* in Figure 7). Note that the differences between Figures 8a, 8b, and 8c are minor, indicating that σ_c^* is relatively independent of the supercooling within the range studied. Hence, the comparison in Figure 8 indicates again that the disagreement between the measured and predicted σ_c^* at higher solute concentrations is not due to convection, since the convection intensity is primarily controlled by the imposed supercooling and actually decreases with increasing solute concentration. As with Figure 7, no explanation for the disagreement is currently available. The systematic nature of the disagreement in Figure 8 points to some problem with the selection theory for alloys.

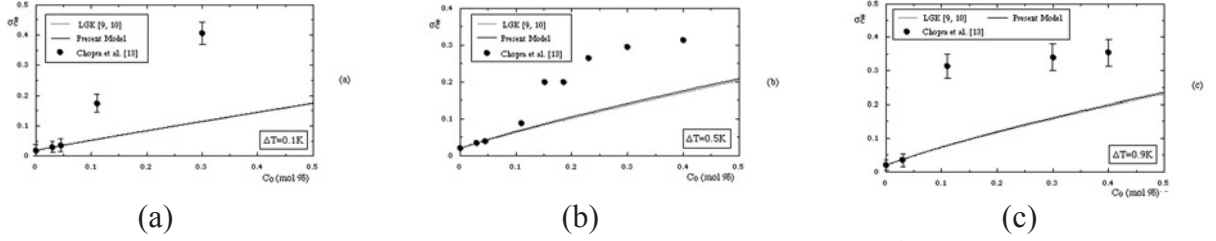


Figure 8. Comparison of the measured and predicted selection parameter σ_C^* , as defined in Eq. (22), as a function of solute concentration for SCN-ACE alloys at (a) $\Delta T=0.1$ K, (b) $\Delta T=0.5$ K, and (c) $\Delta T=0.9$ K.

5.5. Effect of the selection parameter σ^* on the predicted Peclet number

As shown in Figure 7, the measured selection parameters σ^* for higher solute concentrations are significantly different from the 0.02 value used in Section 5.3 (Figures 3 to 6) to assess the present convection model. Therefore, it is useful to examine the effect of σ^* on the predicted thermal Peclet numbers, Pe_T . As mentioned above, σ^* affects the heat and solute transport at the dendrite tip through the dependence of the convection boundary layer thicknesses on the tip radius and, to a lesser extent, through the capillary correction.

Using the measured σ^* values from Figure 7, instead of a constant value of 0.02, the Pe_T numbers are recalculated with the convection model for each of the data points in the experiments of Chopra et al. These modified predicted Pe_T are included as open triangles in Figure 6. It can be seen that the predicted Pe_T using the measured σ^* (open triangles) are somewhat closer to the experimental data (solid circles) than the predicted Pe_T using $\sigma^*=0.02$ (solid line).

At the lowest supercooling of 0.1 K (Figure 6a), when the convection effect is strongest, the present model now shows reasonable agreement with the data over almost the entire solute concentration range. Hence, this comparison can be regarded as a validation of the present convection model.

At the two higher supercoolings of 0.5 K and 0.9 K (Figures 6b and 6c), the use of the measured σ^* in the convection model still cannot explain the low values of the measured Pe_T for higher solute concentrations, although some improvement in the agreement can be noted. Since the convection effect is very small at 0.9 K and, thus, the influence of σ^* on Pe_T is small, the convection model is unlikely to be the reason for these discrepancies.

6. Conclusions

A stagnant film model of thermosolutal convection during free dendritic growth of alloys is developed. The model is based on the standard description of diffusion-controlled free dendritic growth in alloys at low Peclet numbers¹⁹, with the convection effects taken into account through the introduction of thermal and solutal boundary layer thicknesses in the transport solutions for the dendrite tip. The boundary layer thicknesses are evaluated through appropriate Nusselt and Sherwood number correlations for thermosolutal convection that are calibrated using available dendritic growth data for pure SCN. The predictions of the present model are compared to the earth-based experiments of Chopra et al.¹³ for SCN-ACE alloys.

It is found that the convection model gives excellent agreement with the measured dendrite tip velocities and radii of Chopra et al. for low solute concentrations. This is significant because the measured tip velocities are up to a factor of four higher than the predictions of the diffusion model, while the measured tip radii are up to a factor of two lower than the diffusion predictions. However, at higher solute concentrations the present predictions show some deviations from the measured data, and the measured (thermal) Peclet numbers tend to fall even below the predictions from the diffusion theory. It is particularly puzzling that the largest deviations between the measured and predicted Peclet numbers occur at the highest supercooling (0.9 K) where the convection effect is very small. Thus, the convection model is unlikely to be the reason for these discrepancies at higher solute concentrations. It is also shown that the use of the measured selection parameter σ^* , instead of a constant value equal to 0.02, leads to some improvement of the prediction of the measured Peclet numbers, particularly at the lowest supercooling when the convection effect is strongest.

The present comparison of the theories with the experimental data of Chopra et al. also shows that at solute concentrations above 0.1 mol% ACE, the measured selection parameter σ^* is significantly above the expected value of 0.02 and exhibits strong scatter. Similarly, the selection parameter σ_c^* , defined in Eq. (22), is systematically above the theoretical prediction at large solute concentrations. Convection is not responsible for these discrepancies, primarily because the disagreements are independent of the supercooling and because the convection effect becomes weaker with increasing solute concentration.

The above comparisons show that, despite the overall success of the present convection model, available free dendritic growth theories cannot accurately predict all measured dendrite tip velocities and radii in the SCN-ACE experiments of Chopra et al. The persistent disagreements at the highest supercooling (0.9 K) could be caused by experimental difficulties, since the high tip velocities and very small tip radii (of the order of 5 microns) in this regime can lead to a large measurement uncertainty¹⁸. On the other hand, the systematic discrepancies in the selection parameters for higher solute concentrations, even at the lowest supercooling (0.1 K) where the tip radii are relatively large (of the order of 100 microns), is most likely not due to measurement uncertainties. They indicate that the theory for the selection of the dendrite tip operating state in alloys may need to be reexamined.

Acknowledgements

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CONVECTION EFFECTS IN THREE-DIMENSIONAL DENDRITIC GROWTH

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Abstract

A phase-field model is developed to simulate free dendritic growth coupled with fluid flow for a pure material in three dimensions. The preliminary results presented here illustrate the strong influence of convection on the three-dimensional (3D) dendrite growth morphology. The detailed knowledge of the flow and temperature fields in the melt around the dendrite from the simulations allows for a detailed understanding of the convection effects on dendritic growth.

Introduction

Dendrites are the most common microstructure found in engineering materials. The shape, size and orientation of the dendrites determine to a large extent the physical and chemical properties of cast and welded metals. While numerous experimental, numerical and analytical studies have been performed to understand dendritic growth in diffusion-controlled situations¹⁻¹², the pattern selection and microstructure evolution are not well understood for convection-controlled growth. Convection in the melt during solidification can be caused by buoyancy forces, dendrite movement, shrinkage, or a variety of imposed flows.

In the past ten years, the phase-field method¹³⁻¹⁶ has become a popular computational tool to simulate microstructure formation in solidification. The main advantage of the phase-field method is that it avoids direct tracking of the sharp solid-liquid interfaces¹⁷⁻¹⁹. Based on an analysis of the thin interface limit, Karma and Rappel²⁰⁻²² proposed a computationally efficient phase-field method that allows for quantitative modeling of dendritic crystal growth. Beckermann et al.²³ employed the phase-field method to study convective effects on dendritic growth in two dimensions (2D). The numerical results show that convection can significantly alter the operating state of a dendrite and dendritic sidebranching. Very recently, Jeong et al.²⁴ investigated the effect of fluid flow on 3D dendritic growth using an adaptive-grid finite element method. They found that the flow and dendrite growth shapes in three dimensions are very different from those in two dimensions.

In this paper, our previous simulations of 2D dendritic growth with convection²³ are extended to three dimensions. Preliminary results are presented that illustrate the effects of convection on dendritic growth.

Governing equations

The governing equations for flow and heat transfer are the same as those derived in Ref.²³, while the phase-field equation is taken from the work of Karma and Rappel²⁰⁻²². The effects of flow in the phase-field equation are neglected. All equations are valid in the single-phase solid and liquid regions as well as in the

Keywords: dendritic growth, phase-field method, convection, fluid

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diffuse interface region, where the phase-field variable, ψ , varies from -1 to $+1$. An auxiliary variable, the solid fraction ϵ_s , is introduced as $\epsilon_s = (1 + \psi)/2$. The equations can be summarized as follows.

Mass conservation:

$$\nabla \cdot [(1 - \epsilon_s) \cdot \vec{v}_l] = 0, \quad (1)$$

where $\vec{v}_l$ is the intrinsic velocity of the liquid.

Momentum conservation:

$$\begin{aligned} \frac{\partial}{\partial t} [(1 - \epsilon_s) \vec{v}_l] + \nabla \cdot [(1 - \epsilon_s) \vec{v}_l \vec{v}_l] = & -(1 - \epsilon_s) \nabla p \\ & + v_l \nabla^2 [(1 - \epsilon_s) \vec{v}_l] - v_l \frac{h \epsilon_s^2 (1 - \epsilon_s)}{W_0^2} \vec{v}_l, \end{aligned} \quad (2)$$

where v_l , p , and t are the kinematic viscosity, pressure, and time, respectively. The parameter W_0 is representative of the interface thickness (see below). The last term on the right-hand side of equation (2) is a distributed interfacial force term that forces the liquid velocity to vanish across the diffuse interface as the solid approached. The coefficient h is a constant equal to 5.514, which was determined from an asymptotic analysis that forces the velocity profile to approach that for a no-slip condition at a sharp interface located at $\epsilon_s = 0.5$.

Energy conservation:

$$\frac{\partial u}{\partial t} + \nabla \cdot [(1 - \epsilon_s) v_l u] = D \nabla^2 u + \frac{\partial \epsilon_s}{\partial t} \quad (3)$$

where D is the thermal diffusivity. The dimensionless temperature u is defined as $u = (T - T_M)/(L/c_p)$, where T_M , L , and c_p are the melting temperature, latent heat, and specific heat at constant pressure, respectively.

Phase-field equation:

$$\tau(\mathbf{n}) \frac{\partial \psi}{\partial t} = [\psi - \lambda u (1 - \psi^2)] (1 - \psi^2) + \nabla \cdot [W^2(\mathbf{n}) \nabla \psi] + \sum_{\xi=x,y,z} \frac{\partial}{\partial \xi} \left[|\nabla \psi|^2 W(\mathbf{n}) \frac{\partial W(\mathbf{n})}{\partial (\partial_\xi \psi)} \right], \quad (4)$$

where λ is a dimensionless parameter that controls the strength of the coupling between the phase and temperature fields, and $\mathbf{n}$ is the interface normal. The interface thickness parameter W depends on the orientation of the interface and is given by $W(\mathbf{n}) = W_0 a_s(\mathbf{n})$. In the limit of vanishing interface kinetics, $\tau(\mathbf{n})$ is chosen as $\tau(\mathbf{n}) = \tau_0 a_s^2(\mathbf{n})$, with

$$a_s(\mathbf{n}) = (1 - 3\epsilon_4) \left[1 + \frac{4\epsilon_4}{1 - 3\epsilon_4} \frac{(\partial_x \psi)^4 + (\partial_y \psi)^4 + (\partial_z \psi)^4}{(\nabla \psi)^4} \right], \quad (5)$$

where ϵ_4 is the anisotropy strength. All other details can be found in the original references.^{18, 19}

Numerical method

The energy and phase-field equations are solved using an explicit finite difference method on uniform grids that are different from each other. The node spacing for the energy equation is exactly twice as large as the one for the phase-field equation, as illustrated in Figure 1. This can be done without loss of accuracy, because the thermal diffusion length is much larger than the diffuse interface thickness. The temperatures on the fine-mesh nodes for use in the phase-field equation are obtained by linear interpolation. Extensive numerical tests were performed to validate this approach for the ranges of the governing parameters considered here.

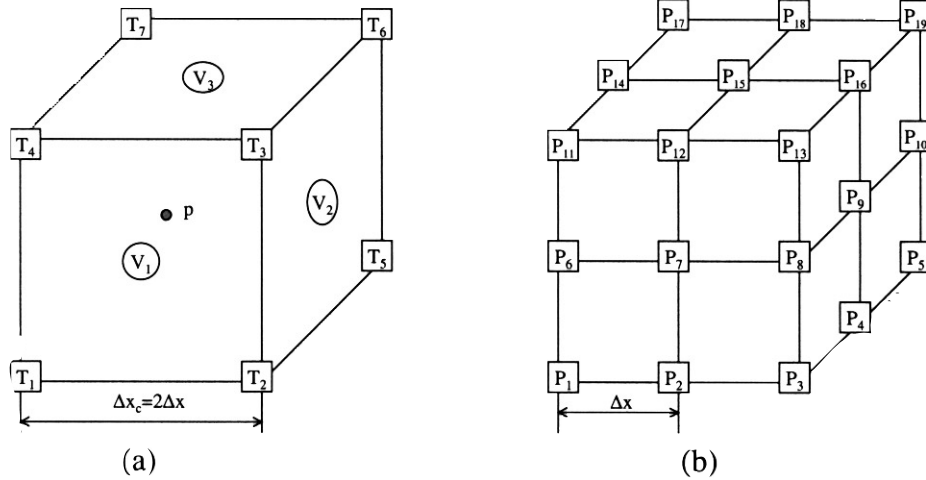


Figure 1. Configurations in the fine and coarse meshes. (a). One coarse grid (big cube) in finite difference scheme (or one element in finite element scheme). Nodes for temperature are defined on 8 corners, namely $T_1 \sim T_8$ (T_8 is not shown in the Figure). Nodes for velocity are defined on the 6 surface centers of the coarse grid, namely $V_1 \sim V_6$ ($V_4 \sim V_6$ are not shown in the Figure). Pressure p is defined on the volume center of the coarse grid. (b). 8 fine grids (cubes) that correspond to one coarse grid. Nodes for the phase-field variable are defined on every corner of the fine grid, namely $P_1 \sim P_{27}$ ($P_{20} \sim P_{27}$ are not shown for clarity).

The mass and momentum equations are solved using a modified version of the finite element CFD code FEAST²⁵. This code was originally developed by Turek and coworkers in the Department of Mathematics at the University of Dortmund, Germany. Descriptions of the discretization technique, the error control method, and the multi-grid solution scheme can be found online²⁵. The code was modified to accommodate the non-standard forms of the mass and momentum equations, Eqs. (1) and (2). As shown in Figure 1a, the velocity is defined at the center of the six surfaces of the element, while the pressure is defined at the center of the volume element. Most importantly, the element edge length is again twice as large as the node spacing used in the solution of the phase-field equation. Since most of the total computational effort is associated with the solution of the flow equations, this method offers tremendous savings in both computer time and memory. It was verified through extensive numerical tests that the use of a coarser mesh for the flow equations does not sacrifice accuracy for the cases considered here. The velocities were interpolated to the appropriate locations for use in the solution of the energy equation. The flow equations are solved in a fully implicit manner. As found previously by the present authors²³, this allows for the use of a larger time step (about five times as large) for the flow equations than for the phase-field and energy equations; however, this procedure was not utilized in the present study.

Numerous benchmark problems were solved using the present 3D code in order to validate the numerical method. Only one of these, flow around a cylinder at low Reynolds numbers, is described here. The cylinder was represented by a (stationary) distribution of the phase field variable, which varies in a hyperbolic tangent fashion across the cylinder-fluid interface. In other words, the cylinder was not explicitly discretized. For the present simulations at low Reynolds numbers, the computational domain has to be much larger than the cylinder so that the flow field is not influenced by the boundaries²⁶; hence, a non-uniform grid of hexahedral elements was utilized. A two-dimensional cut of the mesh is plotted in Figure 2a. Since the elements are densely concentrated at the center of the cut where the cylinder is present,

an enlarged view of this region of the mesh is shown in Figure 2b. The flow is from left ($x=0$ plane) to right ($x=10$ plane) in this Figure. A uniform inlet velocity and a zero-velocity gradient at the outlet are used as boundary conditions on these two planes. Slip boundary conditions are applied at the bottom ($y=0$ plane) and top ($y=10$ plane) boundaries. Two-dimensional results for an infinitely long cylinder are desired for the comparison with the benchmark results. Hence, slip boundary conditions are applied on the front and back boundaries. Then, the size of the domain in the z -direction (parallel to the axis of the cylinder) is arbitrary.

Using the computed flow results, the drag coefficient, C_D , of the cylinder was determined as a function of the Reynolds number. A comparison of the present results for the drag coefficient with previous experimental measurements²⁷⁻²⁸ is shown in Figure 3. The agreement is good for all Reynolds numbers.

Results

Figure 4 shows the physical domain and conditions used in the present simulation of free dendritic growth in the presence of melt convection. A spherical seed at the melting temperature ($u=0$) is located in the center of a cubic domain of volume 204.8^3 . The $[100]$, $[010]$ and $[001]$ crystalline directions are aligned with the x , y , z coordinates, respectively. Undercooled melt enters the domain at the $x=0$ plane with a uniform velocity of $U=1$ and dimensionless temperature of $u_{in}=\Delta=-0.55$. The melt exits at the opposing end of the domain. Symmetry or slip boundary conditions are imposed on the four planes normal to the inlet and outlet. For the present low Reynolds number flow, symmetry allows the computations to be performed in only a quarter of the domain. Other conditions include $D=4$, $\varepsilon_4 = 0.05$, and $Pr = \nu/D = 2.5$. The calculations were performed on a uniform grid of $128 \times 64 \times 64$ nodes for the flow and temperature fields and of $256 \times 128 \times 128$ nodes for the phase field.

Figure 5 shows computed dendrite shapes at various times. Since the dendrite would be completely symmetric in the absence of flow, it is obvious that the convection dramatically alters the growth morphology. The arms growing into the flow, in the upstream direction, grow much faster than the cross-stream arms. The arm pointing in the downstream direction grows so slowly that it is virtually non-existent.

The flow field is illustrated in Figures 6 to 8. Figure 6 shows the general characteristic of the streamlines around the dendrite. Figures 7 and 8 show representative streamlines on the upstream and downstream sides of the dendrite, respectively. The flow advects heat from the upstream to the downstream side. Consequently, the temperature field around the dendrite is very asymmetrical, as shown in Figure 9. The temperature gradients are largest at the upstream tip, resulting in the large growth velocities there. The temperature in the wake of the dendrite is more uniform and closer to the melting point. Compared to the downstream arm, the cross-stream arms suffer much less from the convective transport of heat. This can be seen from the streamlines in Figures 6 to 8. Most of the fluid that passes near the upstream dendrite arm and gets heated, flows through the space between the four cross-stream arms. The melt that passes directly by the cross-stream arm tips originates primarily from the far field and is not heated by any upstream structure. As can be seen from Figure 6, the shape of the cross-stream arm is very asymmetrical in the z plane, which again is caused by advection of heat around those arms.

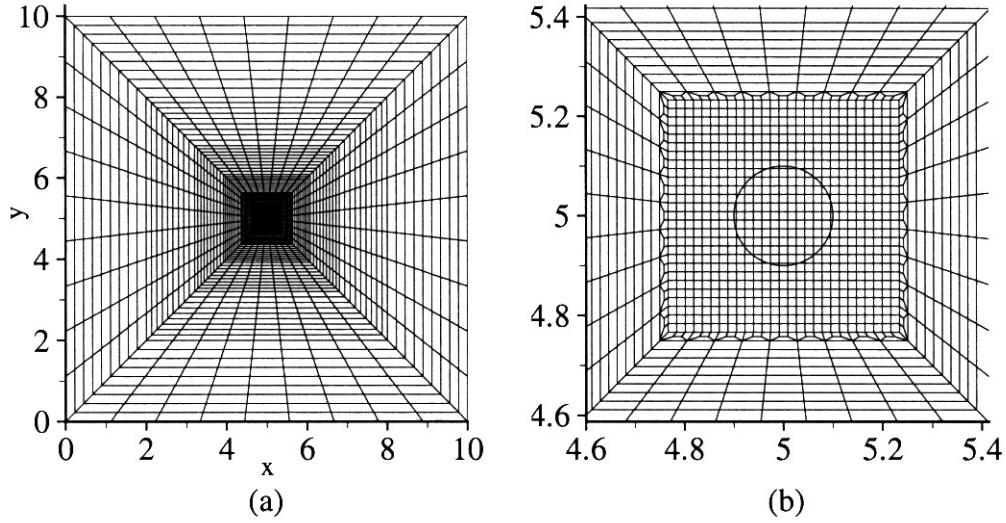


Figure 2. 2D view of the non-uniform mesh for calculating the cylinder drag at low Reynolds numbers. 3D mesh is simply extended by this 2D mesh in the z direction. The domain size is $10 \times 10 \times 0.8$. (a). Complete 2D view of the mesh. (b). Better view of the 2D mesh in the center region of the domain. The circle (cylinder in 3D) is defined by a (stationary) distribution of the phase-field variable, which varies in a hyperbolic tangent fashion.

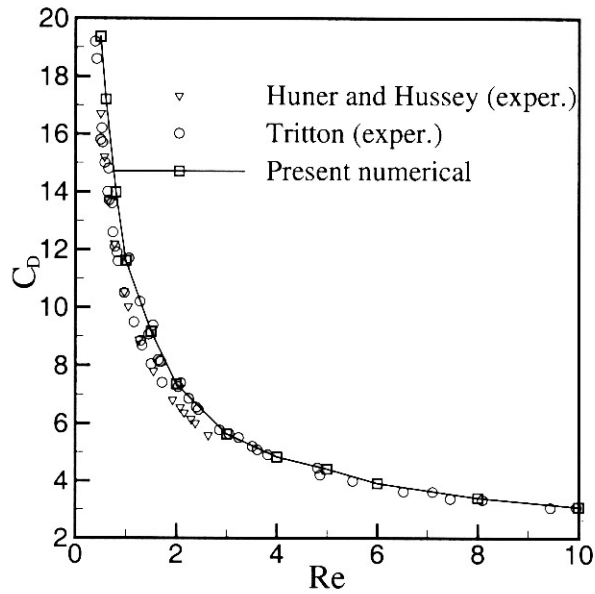


Figure 3. Cylinder drag coefficient at low Reynolds numbers.

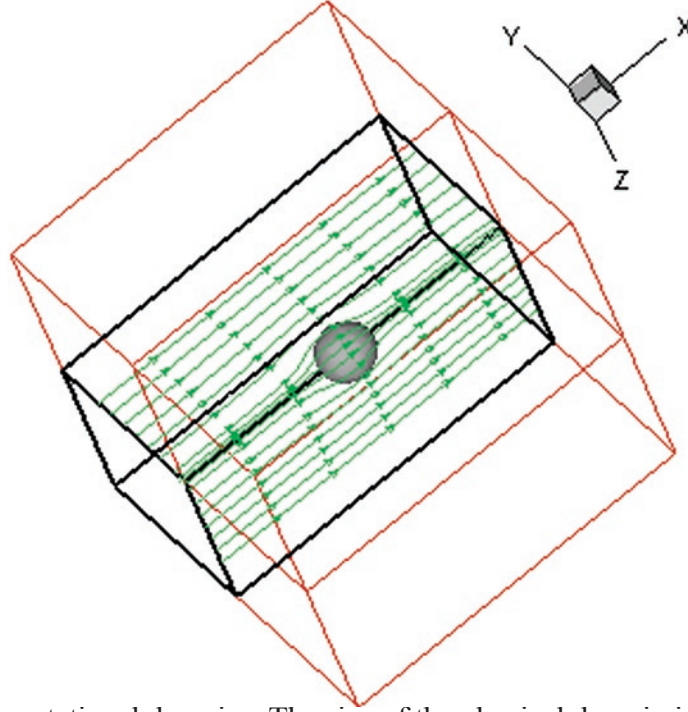


Figure 4. Physical and computational domains. The size of the physical domain is 204.8^3 . The computation domain is only one quarter of the physical domain (the first octant with black color) due to symmetry. Fluid with uniform velocity ($U=1$) passes over the sphere seed initially fixed in the center of the physical domain.

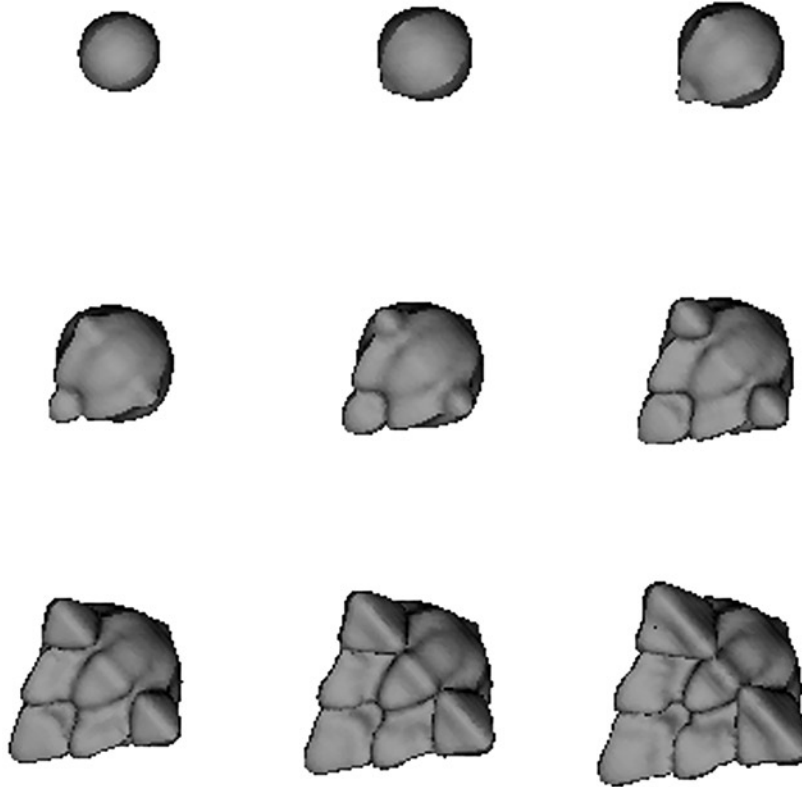


Figure 5. Microstructure evolution of the dendrite under convection. The dimensionless time interval is $\Delta t/\tau_0 = 8$. The input parameters are $\Delta = -0.55$, $D=4$, $\varepsilon_4 = 0.05$, $Pr = \nu/D = 2.5$, $U=1$, and $\lambda = 6.383$.

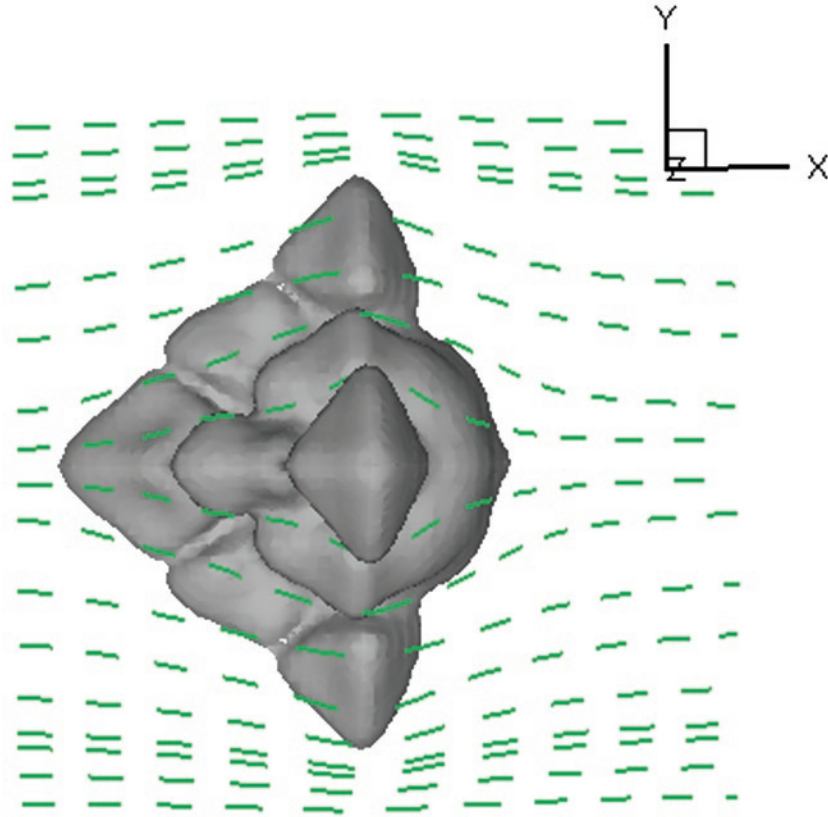


Figure 6. Streamlines around the dendrite viewed in z direction.

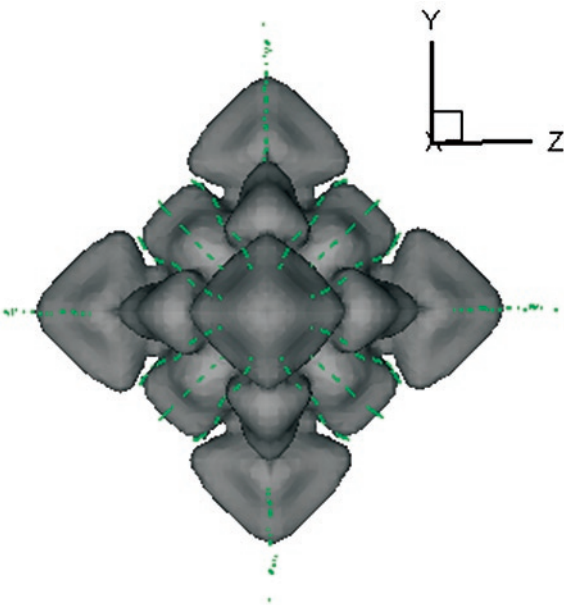


Figure 7. Streamlines near the upstream arm viewed from negative x direction

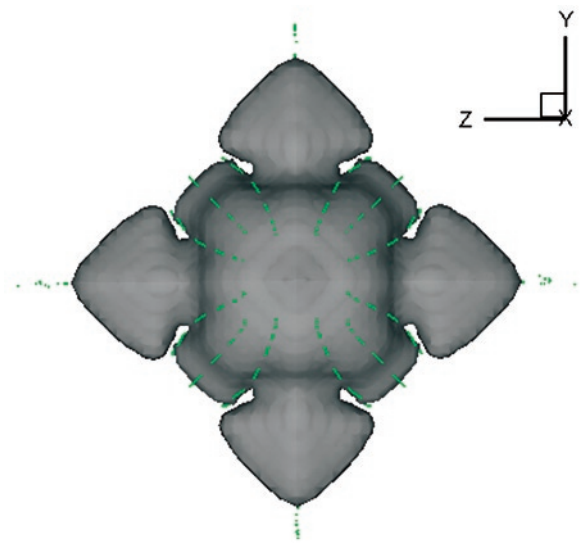


Figure 8. Streamlines near the downstream arm viewed from positive x direction

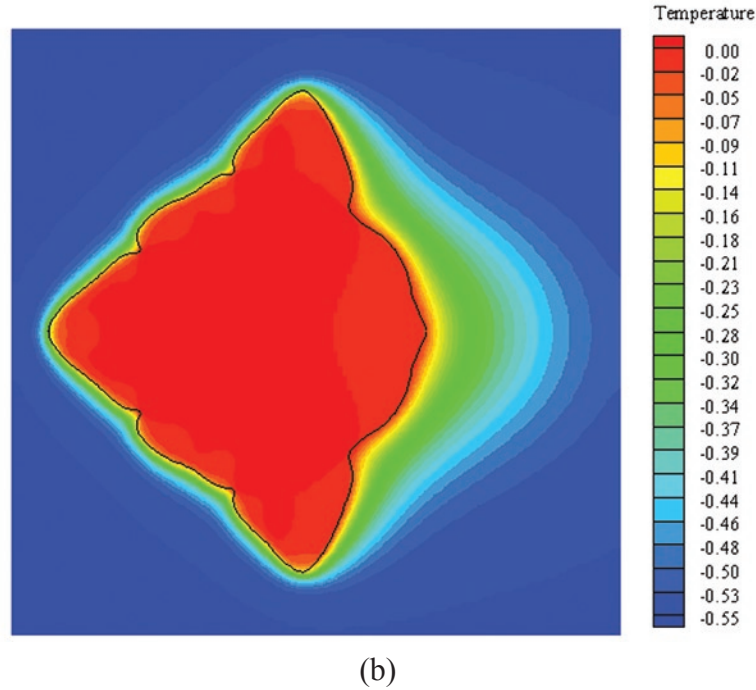
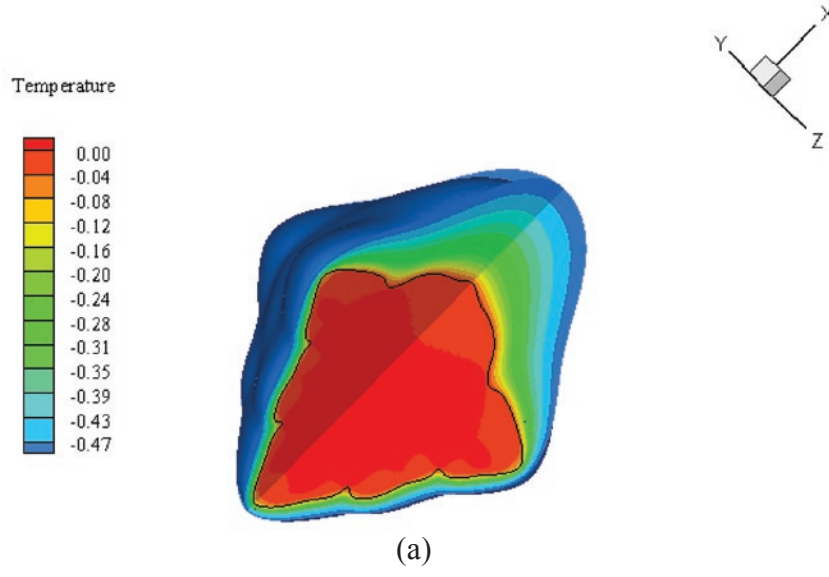


Figure 9. Temperature field around the dendrite. The black line represents the interface contour. (a). 3D temperature field around the dendrite. The first octant was cut for better visualization. Temperature below -0.47 was not shown for clarity. (b). 2D temperature field at $y=0$ plane.

Conclusions

A phase-field method has been developed to simulate free dendritic growth in three dimensions in the presence of a forced melt flow. Convection is found to significantly alter the growth morphology of dendrites. While the flow and temperature results presented here allow for a qualitative understanding of the effects of convection, a comparison of the predictions with relevant dendrite growth theories and experimental results is still underway.

Acknowledgements

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NUMERICAL AND EXPERIMENTAL INVESTIGATION OF THE SOLIDIFICATION OF A BOTTOM CHILLED CAVITY

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The solidification of a bottom-chilled cavity filled with ammonium chloride is investigated in this work. The velocity field near the mushy region is measured and compared to computed results to improve on porosity models. This investigation also attempts to determine the suitability of two novel techniques, one experimental and one numerical, for studying solidification processes. A finite element/fictitious domain method is implemented to evaluate the performance of this approach for solidification problems. Experimental investigations to measure the velocity fields at various instants are carried out using Molecular Tagging Velocimetry (MTV).

The fictitious domain method is well suited for rapid design since it eliminates the need for a boundary conforming mesh. In this technique, the domain of the original problem is extended to a larger and simpler auxiliary domain with periodic boundary conditions. Lagrange multipliers are then used to enforce the original boundary conditions. This approach gives rise to efficient numerical scheme, but increases the memory requirements. Simple problems are solved to illustrate the methodology.

The MTV method was used to measure the velocity field directly above the chimneys and the adjacent mushy zone. Efforts are currently underway to measure both temperature (using laser induced fluorescence or LIF) and velocity fields simultaneously, as well as reducing the cavity size. The use of MTV/LIF will provide novel experimental results spanning various cavity sizes and chilled configurations. This will demonstrate the capabilities of the MTV/LIF method, provide verification of the modeling approaches proposed, and provide benchmark velocity and temperature field data valuable to other analytical and numerical studies, as well as enhance our understanding of thermo-solutal convection processes. Efforts to obtain micro-scale field measurements around the mushy zone are currently under way.

Keywords: molecular tagging velocimetry, finite elements, fictitious domain

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KINETIC EVOLUTION OF STABLE AND METASTABLE STATES OF PROTEIN SOLUTIONS

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The thermodynamic and kinetic properties of protein solutions are important in many industrial, scientific and pathophysiological applications. These applications include the large scale separation of proteins by aqueous two phase partition and the production of crystals of biologically important proteins for the determination of their three-dimensional structure.^{1,2} Protein solutions exhibit phase transformations such as crystallization, metastable liquid-liquid phase separation, aggregation, self assembly and gelation. We have investigated the crystallization and metastable liquid-liquid phase separation (LLPS) in the γ crystallins, a family of proteins of eye lenses.³ In crystallization, a solid (crystal) forms from the protein solution. In LLPS, the solution separates into two coexisting liquid phases of unequal protein concentration. This LLPS is brought about by the attractive interactions between the γ crystallins.⁴ Although LLPS is metastable with respect to crystallization, crystal formation in the γ crystallins is usually slow enough so that the coexistence curve can still be measured. We have analyzed the effect of protein modifications (genetic mutations) and the effect of additives (PEG) on the phase behavior of γ crystallins aqueous solutions.

The formation of new phases is known to be strongly influenced by the phenomena of gravity-driven convection and sedimentation. This is especially true for proteins, since they are large particles with slow kinetic behavior. Under microgravity conditions the effects of convection and sedimentation are greatly reduced, and thus transformations which are usually masked by the presence of gravity can be observed. Microgravity conditions can elucidate the variety of condensed phases possible in protein solutions.²

The Effect of Protein Modifications on the Phase Behavior of Protein Solutions

We have used bovine γ B crystallin as a model system to study the role of individual cysteine residues in the phase separation of the γ crystallins. We compare the thermodynamic and kinetic behavior of recombinant wild type protein (WT) and the Cys 18 to Ser mutant (C18S).⁵

We determined the solubilities and the liquid-liquid coexistence curves of WT and C18S. Unexpectedly, the mutant protein forms crystals much more quickly than the wild-type protein. C18S crystallizes in a matter of hours, while it takes days or even weeks for crystals of WT to form. Both proteins form crystals of similar shape and size. The rapid crystallization of C18S is caused by an enhanced nucleation rate and not by a faster growth rate; when solutions of WT are seeded with WT crystals, crystal growth occurs at the same rate as in solutions of C18S seeded with C18S crystals. It is interesting to note that cross-seeding is not effective. Crystals do not grow in solutions of WT seeded with C18S crystals. The slow crystallization allows the liquid-liquid coexistence curves of the WT to be readily determined and they

Keywords: crystallization, liquid-liquid phase separation, PEG, γ crystallin, kinetics, theoretical

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are identical. The rapid crystallization of C18S, however, renders a direct measurement of its coexistence curve impossible. An indirect determination of the location of the C18S coexistence curve is possible if the crystallization of the protein is suppressed. We have found that in solutions of C18S which contain 5% of WT, the crystallization of C18S is delayed by approximately 24 hrs as compared to pure solutions of C18S at the same total protein concentration. The crystals which do eventually form in this mixture consist of pure C18S. In solutions with 10% of WT, crystallization is not observed at all. In Fig. 1, we can see that the coexistence curves of C18S mixtures with 5% (triangles) and 10% (squares) of WT coincide with that of the pure WT protein (circles). From this we deduced that the coexistence curve of pure C18S coincides with that of WT. This result is not surprising given that liquid-liquid phase separation is mainly governed by the average energy of interaction between the proteins, and the conservative mutation introduced should barely alter this average energy.

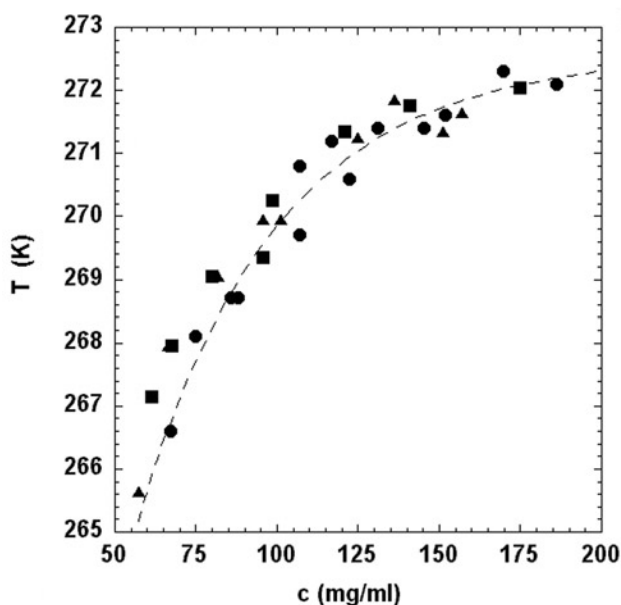


Figure 1. Coexistence curves for the aqueous (0.1 M phosphate buffer pH 7) WT system (●), C18S (95%)–WT (5%) system (▲) and C18S (90%)–WT (10%) system (■). The dashed curve is a guide for the eye. c (mg/ml) is the protein concentration and T (K) is the temperature. The LLPS temperatures were determined by the transmitted intensity method.⁶

The enthalpies (ΔH) of crystal formation provide a quantitative measure of the similarity between the interactions of the proteins. These enthalpies may be extracted from the slope of the solubility curves using the van't Hoff equation.⁷ In Fig. 2, we show the solubility curves of WT (circles) and C18S (triangles). To within the experimental error, the enthalpies of crystal formation of WT and C18S are identical (see Fig. 2).

Why does C18S crystallize so much more rapidly than WT? One possibility is that the mutant and wild-type proteins have different crystal forms. It is well known that different crystal forms nucleate at different rates.⁸ We determined the space groups and unit cells of the C18S and WT crystals to check if they were the same. We also compared the x-ray structures of the two proteins to verify that the mutation had not significantly affected the three dimensional structure of the protein, and thus demonstrate that the altered kinetics were not due to a major conformational change in the protein. Several instances of amino acid substitutions leading to increased crystal nucleation rates have been reported. The rationales included strengthening or introducing a crystal contact, constructing the building blocks of the crystal (e.g. forming

dimers out of a monomeric protein for which it is known that the asymmetric unit in the crystal is a dimer) and suppressing aggregation by removing a reactive residue, generally a cysteine. None of these rationale

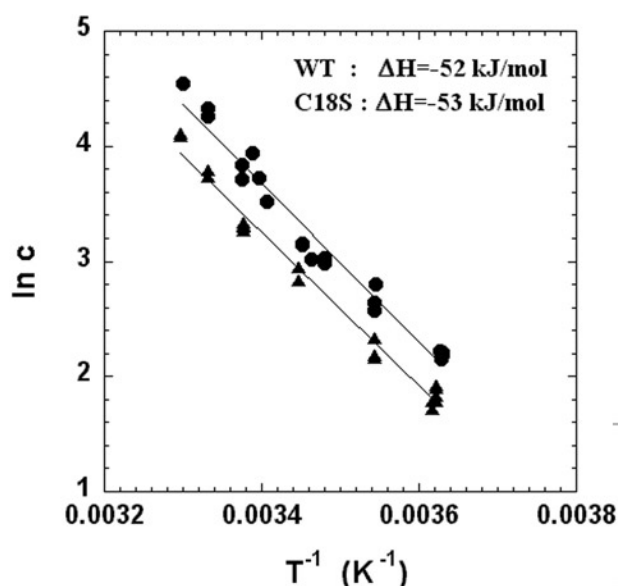


Figure 2. Solubility curves for the aqueous WT system (●) and C18S system (▲). The solid lines are fit to the experimental results. c (mg/ml) is the protein concentration and $T(K)$ is the temperature. The enthalpies (ΔH) of crystallization are obtained from the slope of the solubility curves using the van't Hoff equation.

explain the enhanced nucleation of the C18S mutant. The Cys18 residue is not at a crystal contact and the asymmetric unit of the crystal is a monomer. Furthermore, the enhanced nucleation was observed under reducing conditions; the solutions of WT and C18S remained essentially monomeric over the course of the crystallization experiments. The inability of C18S and WT to co-crystallize is also intriguing. Proteins which are as similar as C18S and WT generally co-crystallize and co-crystallization has been reported for pairs of proteins which are fairly different in structure.⁹ It is also surprising that C18S did not act as a seed for WT. Cross-seeding of proteins is usually successful with similar proteins and often works with proteins which do not resemble each other as much as C18S and WT do. The absence of co-crystallization suggests that it is the C18S alone that is involved in nucleation. Nevertheless, the observed reduction in nucleation rate found in the mixtures is much more than expected from classical nucleation theory.¹⁰ According to this theory, the nucleation rate is proportional to the probability of producing a critical nucleus of n proteins. This probability contains a factor of c^n , where c is the concentration in solution of the nucleating species. The presence of inert WT in the mixtures simply reduces c by dilution. According to this picture, the observed halving of the nucleation rate in the 5% mixture (as compared to pure C18S) implies that $n = \ln(1/2)/\ln(0.95) \approx 14$. Although this is a reasonable size for a critical nucleus of a protein crystal, this value of n implies that for the 10% mixture, there should be only about a four-fold reduction in nucleation rate. The actual nucleation rate dropped by more than fourteen-fold. This discrepancy illustrates the limitations of classical nucleation theory when applied to protein solutions.

Our work shows that even a conservative point mutation in a protein can produce an order of magnitude increase in the rate of crystallization. This increase occurred without any change in the solubility of the protein, the crystal form, or the protein conformation in the crystal. According to conventional criteria, the enhanced nucleation of C18S crystals should involve one or more of the following factors: a crystal contact, the formation of the asymmetric unit, or the suppression of aggregation. Our data shows that

the increase in the rate of crystallization of C18S does not involve any of these factors. Unraveling the mechanism underlying the enhancement of nucleation in C18S may prove valuable in the crystallization of other proteins.

The Effect of PEG on the Phase Behavior of Protein Solutions

We have investigated the effect of small polymers on the metastable LLPS of protein solutions. Our research is motivated by the extensive practical use of PEG as a precipitating agent and in two phase partition.^{1,2} We have used bovine γ D crystallin (γ D) as a model system to study effect of low molecular weight (200-3350Da) PEG on the liquid-liquid transition of protein systems. LLPS is not only a powerful tool for the analysis of protein-PEG interactions, but the role of the liquid-liquid phase boundary itself is believed to be relevant to the protein crystallization kinetics.¹¹

The LLPS properties of the protein-PEG-water ternary system are described by a coexistence surface in the phase diagram. This coexistence surface represents the LLPS temperature, as a function of protein concentration, c_1 , and PEG concentration, c_2 . At fixed temperature, the LLPS properties of the system are described by an isothermal coexistence curve, which gives the concentrations (c_1^I, c_2^I) and (c_1^{II}, c_2^{II}) of the coexisting phases, I and II. The partitioning of the components in the two coexisting phases is described by tie-lines connecting the points (c_1^I, c_2^I) and (c_1^{II}, c_2^{II}) of the coexistence curve. The critical point, (c_1^c, c_2^c) , is defined as the point of the coexistence curve where the condition $(c_1^I, c_2^I) = (c_1^{II}, c_2^{II})$ occurs. The location of this point as a function of the temperature is described by a critical line on the coexistence surface.

We describe the composition of the γ D-PEG-water systems by the protein concentration c_1 , and the PEG concentration inside the protein-free volume, c_{2s} . If v is the protein specific volume and $\phi = c_1 v$ is the protein volume fraction, then c_{2s} is equal to $c_2/(1-\phi)$. The choice of c_{2s} instead of c_2 to present our results is justified by the following argument. We consider as a reference system one in which the particles of component 2 have a negligible size and do not introduce specific chemical interactions in the system. In this reference case, the difference in c_2 between two coexisting phases is only related to the exclusion of component 2 to the volume occupied by component 1, which is equivalently expressed by the condition: $c_{2s}^I = c_{2s}^{II}$. Thus, in our systems, any observed difference in c_{2s} between two coexisting phases is related to the finite size and specific chemical properties of the PEG molecules.

In Fig. 3, we present our measurements of the LLPS temperature, T_{ph} , for γ D-PEG-water ternary solutions at constant PEG concentration of $c_{2s} \approx 50$ mg/ml and with several polymer average molecular weights: 200 g/mol (closed squares), 400 g/mol (circles), 1000 g/mol (rhombus), 1450 g/mol (upright triangles), 3350 g/mol (inverted triangles). We also report measurements of temperature of phase separation for the γ D-TEG-water at the same value of c_{2s} (open squares). TEG essentially has the same molecular weight as PEG200, but, in contrast to PEG, is monodisperse. We see from the figure that the two sets of measurements, for TEG and for PEG200, overlap within the experimental error and conclude that the polydispersity effects are small. In Fig. 3, we also show the coexistence curve for the binary aqueous proteins system (dashed curve). The phase transition boundaries of the ternary systems are located at higher T_{ph} than the binary coexistence curve and the difference increases with PEG molecular weight. The critical points, shown by vertical bars in Fig. 3, were identified by the absence of hysteresis in the transmitted intensity-temperature profile.⁶ In all cases, the protein critical concentration value of about 290 mg/ml, is not affected by PEG within the experimental error. On the other hand, the slope of T_{ph} at the critical point, $(\partial T_{ph}/\partial c_1)^{c_{2s}}$, is positive and increases with the PEG molecular weight, in contrast with the zero slope required for the protein-water binary system. In Table 1, we report the values of the PEG concentration, c_{2s} , the critical temperature, T_c and the slope $(\partial T_{ph}/\partial c_1)^{c_{2s}}$.

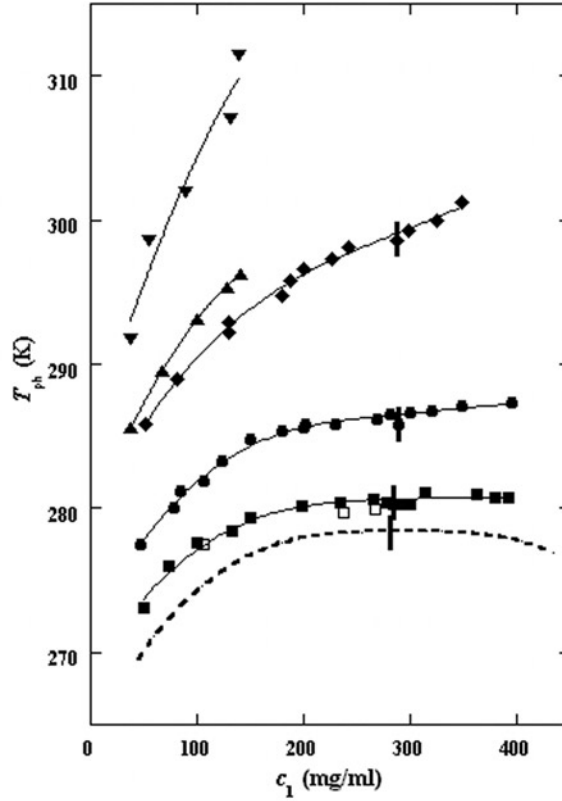


Figure 3. LLPS temperature at constant PEG concentration of 50 mg/ml for the γ D-PEG-water ternary system (0.1M phosphate buffer pH 7). The average molecular weights are: 200 g/mol ($\blacksquare$), 400 g/mol ($\bullet$), 1000 g/mol ($\blacklozenge$), 1450 g/mol ($\blacktriangle$), 3350 g/mol ($\blacktriangledown$). The solid curves are guides for the eye. The values for the γ D-TEG-water ternary system are represented by open squares ($\square$). In the same figure, we draw the coexistence curve for the γ D-water binary system (dashed curve). The vertical bars ($|$) locates the critical point. The LLPS temperature were determined by the transmitted intensity method.⁶

In Fig.4, we present our experimental data (solid circles) of the coexisting values (c_1^I, c_{2s}^I) and (c_1^{II}, c_{2s}^{II}) for the γ D-PEG-water solutions. Since the protein critical concentrations, c_1^c , is equal to the average concentration $(c_1^I + c_1^{II})/2$ in the limit of $c_1^I - c_1^{II} = 0$, we determine c_1^c by plotting $(c_1^I + c_1^{II})/2$ as a function of $c_1^I - c_1^{II}$. The resulting values of the protein critical concentrations (vertical bars in Fig. 4) are, within the experimental error, the same as the value reported for the protein-water system.³ An interesting feature of the phase diagram is the difference of PEG concentration between the two coexisting phases, which increases as the PEG molecular weight increases. In order to describe the effect of PEG molecular weight on PEG partitioning, we consider the normalized slope of the tie-lines at the critical point: $(\partial c_{2s} / \partial c_1)^{c_{T_{ph}}} / c_{2s}^c$. This quantity can be obtained by plotting the incremental ratio $(\ln c_{2s}^I - \ln c_{2s}^{II}) / (c_1^I - c_1^{II})$ as a function of $c_1^I - c_1^{II}$ and considering the limit of $c_1^I - c_1^{II} = 0$. In Table 1, we can see that $(\partial c_{2s} / \partial c_1)^{c_{T_{ph}}} / c_{2s}^c$ increases with the PEG molecular weight.

The protein volume fraction in the protein-rich phase is comparable with the protein volume fraction in the crystal. The non-negligible values of PEG concentration of the protein-rich phases reported for the γ D-PEG1000-water system suggest that the crystal phase can accommodate polymer coils with molecular weight equal to or lower than about 1000 g/mol.

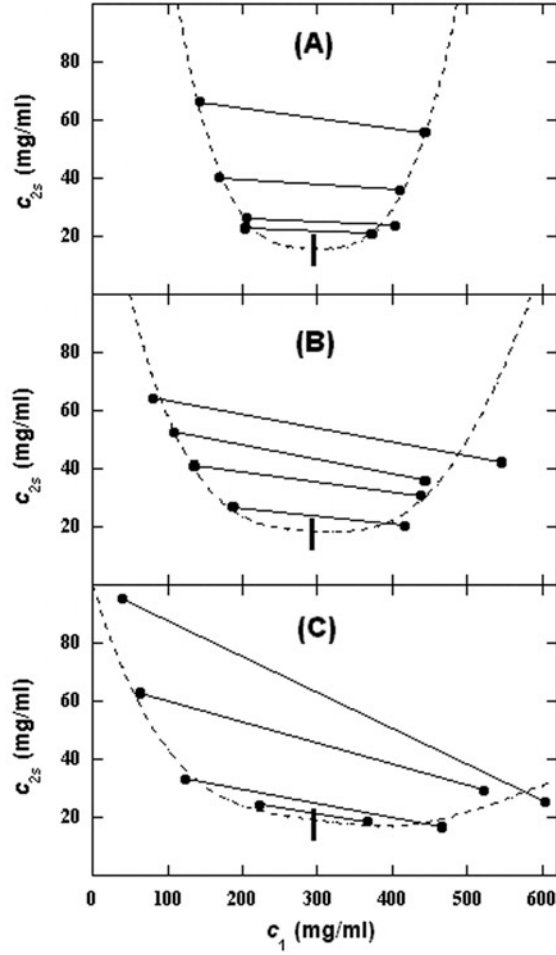


Figure 4. Coexisting surfaces at constant temperature for the γ D-PEG-water ternary system (0.1M phosphate buffer pH 7). The PEG average molecular weights are: 200 g/mol (279.2 K, case A), 400 g/mol (281.7 K, case B) and 1000 g/mol (290.3 K, case C). The pairs of points representing the coexisting phases ($\bullet$) are connected by the tie-lines (solid lines). The dashed curves are guides for the eye and the vertical bars (|) locates the critical point. The protein concentration in each of the coexisting phases was determined by UV absorption. The PEG concentration in each of the coexisting phases was determined by refractive index.

The behavior of the coexistence surface, is described by the three slopes $(\partial c_{2s}/\partial c_1)_{T_{ph}}$, $(\partial T_{ph}/\partial c_{2s})_{c_1}$ and $(\partial T_{ph}/\partial c_1)_{c_{2s}}$, which are related to each other by the mathematical relationship:

$$\left(\frac{\partial T_{ph}}{\partial c_1} \right)_{c_{2s}} = - \left(\frac{\partial T_{ph}}{\partial c_{2s}} \right)_{c_1} \left(\frac{\partial c_{2s}}{\partial c_1} \right)_{T_{ph}} \quad [1]$$

We apply Eq. 1 on the critical line of the coexistence surfaces. Since the critical temperature, T_c of the γ D-PEG-water systems (with $c_{2s} \approx 50$ mg/ml) is higher than the critical temperature, T_c^0 of the γ D-water system (Fig. 1), the quantity $(\partial T_{ph}/\partial c_{2s})_{c_1}$ has to be positive. At the critical point, the slope $(\partial c_{2s}/\partial c_1)_{T_{ph}}$ of the coexistence surface is negative because it coincides with the slope of the tie-lines (Fig. 4). Eq. 1, thus, shows that the slope $(\partial T_{ph}/\partial c_1)_{c_{2s}}$ is positive (Fig. 4 and Table 1) because $(\partial T_{ph}/\partial c_{2s})_{c_1}$ is positive and $(\partial c_{2s}/\partial c_1)_{T_{ph}}$ is negative. The slope $(\partial T_{ph}/\partial c_{2s})_{c_1}$ can be calculated, by using Eq. 1, from the values of c_{2s} , $(\partial T_{ph}/\partial c_1)_{c_{2s}}$ and $(\partial c_{2s}/\partial c_1)_{T_{ph}}$ reported in Table 1. The calculated values of $(\partial T_{ph}/\partial c_{2s})_{c_1}$, which

are also reported in Table 1, are consistent with the dependence of the critical temperature as a function of PEG molecular weight (Fig. 3). We can quantitatively compare the experimental change of critical temperature between the ternary and the binary system, shown in Fig. 3 for each PEG molecular weight, with the change predicted from the calculated values of $(\partial T_{ph}/\partial c_{2s})^c_{c_1}$. In particular, we estimate the critical temperature of the γ D-water system from the expression: $T_c^0 \approx T_c - (\partial T_{ph}/\partial c_{2s})^c_{c_1} c_{2s}$. The calculated values of T_c^0 , which are reported in last column of Table 1, are in acceptable agreement with the experimental value of 278.4 K.³ Thus, by only using the information obtained from the properties of the ternary coexistence surfaces, we are able to estimate the location of the binary liquid-liquid phase boundary. This information can be most useful, when LLPS of protein-water systems is not experimentally observable because it is hidden by the water-ice transition.

Table 1. The values of c_{2s} , T_c , $(\partial T_{ph}/\partial c_1)^c_{c_{2s}}$, $(\partial c_{2s}/\partial c_1)^c_{T_{ph}}/c_{2s}^c$, $(\partial T_{ph}/\partial c_{2s})^c_{c_1}$ and T_c^0 for PEG200 (a), PEG400 (b) and PEG1000 (c).

	c_{2s} mg/ml	T_c K	$(\partial T_{ph}/\partial c_1)^c_{c_{2s}}$ 10^{-3} K mg ⁻¹ ml	$(\partial c_{2s}/\partial c_1)^c_{T_{ph}}/c_{2s}^c$ 10^{-3} mg ⁻¹ ml	$(\partial T_{ph}/\partial c_{2s})^c_{c_1}$ K ⁻¹ mg ⁻¹ ml	T_c^0 K
a	54	280.6	3±2	-0.5±0.1	0.11±0.07	275±4
b	52	286.5	9±1	-1.1±0.1	0.17±0.03	278±2
c	50	299.3	33±3	-2.0±0.3	0.33±0.05	283±3

Thermodynamic description of the system.

We define the quantity F , representing the difference, at constant volume, V , and temperature, T , between the Helmholtz free energy of the virtually incompressible protein-PEG-water system and the pure water system. The changes of F due to the replacement (at constant volume) of γ_1 water moles by one protein mole and γ_2 water moles by one PEG mole are respectively described by the differences of chemical potentials, $\mu_1 \equiv \mu_{\text{protein}} - \gamma_1 \mu_{\text{water}}$ and $\mu_2 \equiv \mu_{\text{PEG}} - \gamma_2 \mu_{\text{water}}$. The quantities μ_1 and μ_2 will be indicated as the protein and PEG effective chemical potentials. It is convenient to describe the thermodynamic of the system by introducing the reduced free energy $\hat{f} \equiv (F - F^0)/RTV$, where F^0 is the standard free energy and R is the ideal gas constant. If the concentration of PEG, c_2 , is relatively small, the reduced free energy is, to first order approximation with respect to c_2 , given by the following equation:

$$\hat{f}(c_1, c_2, T) = \hat{f}(c_1, 0, T) + c_2 \ln(c_2/e) + c_2 \xi(c_1, T), \quad [2]$$

If we differentiate Eq. 2 with respect to the concentrations, c_1 and c_2 , at constant V and T , we obtain the following expressions:

$$\hat{\mu}_1(c_1, c_2, T) = \hat{\mu}'_1(c_1, T) + c_2 (\partial \xi / \partial c_1)_T, \quad [3a]$$

$$\hat{\mu}_2(c_1, c_2, T) = \ln c_2 + \xi(c_1, T), \quad [3b]$$

where, $\hat{\mu}_i \equiv (\mu_i - \mu_i^0)/RT$'s (with $i=1, 2$) are the reduced effective chemical potentials, $\mu_i^0(T) \equiv (\partial F^0 / \partial c_i)_{T,V}/V$ and the quantity $\hat{\mu}'_1(c_1, T) \equiv \hat{\mu}_1(c_1, 0, T)$ is the protein effective chemical potential corresponding to the protein-water binary system.

The slope of the tie-lines.

If we differentiate Eq. 3a with respect to c_2 at constant c_1 and T , and Eq. 3b with respect to c_1 at constant $\hat{\mu}_2$ and T , we obtain:

$$\left(\frac{\partial \hat{\mu}_1}{\partial c_2} \right)_{c_1, T} = \left(\frac{\partial \xi}{\partial c_1} \right)_T = - \frac{1}{c_2} \left(\frac{\partial c_2}{\partial c_1} \right)_{\hat{\mu}_1, T} \quad [4]$$

At the critical point, where the difference between the coexisting concentrations approaches zero, $(\partial c_2 / \partial c_1)_{\hat{\mu}_1, T}$ is equal to the slope of the tie-lines. If we apply Eq. 4 to our experimental tie-lines, we determine that $(\partial \hat{\mu}_1 / \partial c_2)_{c_1, T}$ is positive and increases with the PEG molecular weight. When protein crystals (solid phase) are in thermodynamic equilibrium with the liquid phase, $\hat{\mu}_l$ must be equal to its value in the solid phase, $\hat{\mu}_l^s$. If the protein concentration in the liquid phase is relatively low then $\hat{\mu}_l'(c_1, T) \approx \ln c_1$ and, in condition of chemical equilibrium, Eq. 3a becomes: $\ln c_1 \approx \hat{\mu}_l^s - (\partial \hat{\mu}_1 / \partial c_2)_{c_1, T} c_2$. This last equation describes the behavior of protein solubility as a function of PEG concentration. If the protein crystal has a composition approximately fixed, $\hat{\mu}_l$ is nearly constant and the behavior of the protein solubility is completely described by the value of $(\partial \hat{\mu}_1 / \partial c_2)_{c_1, T}$. In our case, we predict that the protein solubility decreases as c_2 increases, the effect being larger for higher PEG molecular weights. Thus, measurements of tie-lines slopes can be used to predict the dependence of protein solubility on PEG concentration. This is very important for analyzing the effectiveness of a protein precipitating agent such as PEG.

Protein-PEG interactions.

We apply a simple excluded volume model that directly relates PEG partitioning to the difference in free volume fractions between the two coexisting phases. If we assume that PEG molecules can be described as ideal polymer coils and that protein molecules have a spherical shape, then due to steric hindrance, each protein will be surrounded by an adjacent region where the centers of mass of the coils are excluded, and the magnitude, δ , of the resulting depletion layer will be proportional to the gyration radius, R_g , of the polymer coil.¹² If α is the volume fraction available to the centers of mass of the coils, the condition of chemical equilibrium $\hat{\mu}_2(c_1^I, c_2^I, T) = \hat{\mu}_2(c_1^{II}, c_2^{II}, T)$ becomes $c_2^I / \alpha^I = c_2^{II} / \alpha^{II}$, where c_2 / α is the polymer concentration in the free volume and the free volume fraction, α , is equal to $\exp(-\xi)$ (see Eq. 4b).¹³ It has been theoretically shown that, in the case of ideal polymer coils and relatively large hard spheres, $\delta \cong 1.1 R_g$.¹² An approximate expression for the free volume fraction, α , as a function of the hard sphere volume fraction, ϕ , is given by the well established scaled particle theory:¹³

$$\alpha = (1 - \phi) \exp(-A\eta - B\eta^2 - C\eta^3), \quad [5]$$

where $\eta = \phi / (1 - \phi)$, $A = 3q + 3q^2 + q^3$, $B = 9q^2 / 2 + 3q^3$, $C = 3q^3$ and $q = \delta / R$ is the depletion layer thickness normalized with respect to the hard sphere radius, R . Since $c_2^{II} / c_2^I = \alpha(q, \phi^{II}) / \alpha(q, \phi^I)$, we substitute the expression for α provided by Eq. 5 into the ratio of the free volume fractions and thereby determine an *apparent* q value for each experimental tie-line.

In Fig. 5, we present a graph of the apparent q (solid circles) as a function of the square root of PEG molecular weight, together with the theoretical q (open circles), calculated by using $q = 1.1 R_g / R$, where R_g is the PEG gyration radius¹⁴ and R , the γ D equivalent radius, is estimated from the molecular weight and specific volume of the protein. Indeed, the apparent q approximates a linear function of the molecular weight square root, displaying, as expected theoretically, the same behavior as R_g . However, the apparent values of q are about 50% smaller than the corresponding theoretical values. This significant discrepancy represents the deviation of the actual γ D-PEG interactions with respect to the sphere-ideal coil case. Our results suggest the presence of γ D-PEG specific interactions.

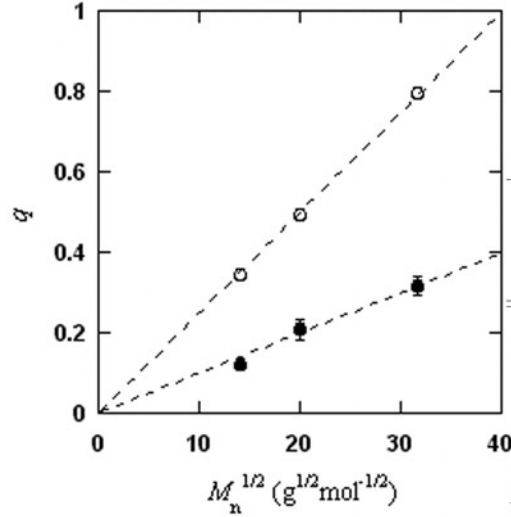


Figure 5. Dependence of the size ratio, q , as a function of the square root of the PEG average molecular weight, M_n . The closed circles (●) are the value obtained by fitting the experimental coexisting compositions with Eq. 2; the open circles (○) are the values calculated by the polymer gyration radii and the protein molecular volume. The dashed lines are guides for the eye.

Stability-instability boundaries. The spinodal surface defines the boundary between the stability domain ($(\partial\hat{\mu}_1/\partial c_1)_{\hat{\mu}_2, T} > 0$) and the instability domain ($(\partial\hat{\mu}_1/\partial c_1)_{\hat{\mu}_2, T} < 0$) of a homogeneous protein-PEG-water system.¹⁵ The spinodal condition, $(\partial\hat{\mu}_1/\partial c_1)_{\hat{\mu}_2, T_{sp}} = 0$, can be used to determine the spinodal temperature, T_{sp} , as a function of c_1 and c_2 . We differentiate Eq. 4a with respect to c_1 at constant $\hat{\mu}_2$ and T , and obtain:

$$\left(\frac{\partial \hat{\mu}_1}{\partial c_1} \right)_{\hat{\mu}_2, T} = \left(\frac{\partial \hat{\mu}_1'}{\partial c_1} \right)_T - \left[\left(\frac{\partial \xi}{\partial c_1} \right)_T^2 - \left(\frac{\partial^2 \xi}{\partial c_1^2} \right)_T \right] c_2, \quad [6]$$

In the case of pure sphere-ideal polymer coil excluded volume interactions, $\alpha = \exp(-\xi)$ and the difference $(\partial \xi / \partial c_1)^2_T - (\partial^2 \xi / \partial c_1^2)_T$ becomes equal to the quantity, $(\partial^2 \alpha / \partial c_1^2)_T / \alpha$. Due to the overlapping of adjacent depletion layers, $(\partial^2 \alpha / \partial c_1^2)_T$ is positive and increases as the depletion layer thickness increases. These general excluded volume concepts can be used to understand the effect of PEG on initially stable protein aqueous solutions. In fact, due to the positive sign of $(\partial \xi / \partial c_1)^2_T - (\partial^2 \xi / \partial c_1^2)_T$, Eq. 6 predicts that as the polymer concentration increases, $(\partial \hat{\mu}_1 / \partial c_1)_{\hat{\mu}_2, T}$ decreases, approaching zero on the spinodal boundary and becoming negative inside the instability domain of the system.

The effect of PEG concentration on the LLPS temperature.

The spinodal surface and the coexistence surface are tangent to each other on the critical line and have qualitatively the same temperature dependence with respect to c_1 and c_2 . If we apply the spinodal condition to Eq. 6 and differentiate the second member with respect to both c_2 and T_{sp} at constant c_1 , we obtain in the limit of $c_2 = 0$:

$$\left(\frac{\partial T_{sp}}{\partial c_2} \right)_{c_1} = \frac{(\partial \xi / \partial c_1)_{T_{sp}}^2 - (\partial^2 \xi / \partial c_1^2)_{T_{sp}}}{(\partial^2 \hat{\mu}_1' / \partial c_1 \partial T_{sp})}, \quad [7]$$

The quantity $(\partial \hat{\mu}_1' / \partial c_1 \partial T_{sp})$ is equal to $-(\partial^2 e' / \partial c_1^2)_T / RT^2$ where e' is the internal energy per unit volume of the protein-water binary system. The quantity $(\partial^2 e' / \partial c_1^2)_{T_{sp}}$ represents the variation of internal energy due to the decrease of the average distance between adjacent protein molecules. Thus, $(\partial^2 e' / \partial c_1^2)_{T_{sp}}$ is negative for 112

attractive protein-protein interactions, zero for hard core interactions and positive for repulsive interactions. Eq. 7, correctly describes the behavior of our experimental results: it predicts that the LLPS temperature increases as the PEG concentration increases, the effect being larger for higher PEG molecular weights. Since colloidal particles can be often treated as hard spheres,¹³ the temperature is usually not considered as a relevant variable for the analysis of colloid-polymer mixtures. On the other hand, we remark that, in the case of protein solutions, where protein-protein interactions are considerably different from the hard sphere case, the LLPS temperature is a powerful tool for the analysis of the nature and magnitude of the protein-protein interactions inside protein aqueous solutions.

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NANOTUBE-BASED STRUCTURES FOR SUPERSTRONG MATERIALS, NANOSCALE SENSORS AND DEVICES, AND EFFICIENT ELECTRON EMITTERS

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Abstract

Carbon nanotubes are one of the most interesting new materials to emerge in the past decade, due to their outstanding mechanical and electrical properties. We have predicted, through large-scale *ab initio* simulations, that they are both incredibly elastic and the strongest materials known. These results have already been confirmed experimentally. However, our most recent calculations, which investigated the atomic transformations leading to fracture, found that the ultimate strength of nanotubes is substantially greater than the one observed experimentally, because in atomically perfect tubes these transformations are hindered by very large barriers. Due to their strength, low specific weight, and unusual electronic properties, nanotube-based materials will enable a variety of unique space and terrestrial applications: in superstrong fibers and composites, as strain and molecular sensors, in novel field emitters, and ultimately in nanoscale electronic devices. Our most recent investigations focus on battery applications, pyro- and piezo-electric nanotubes, and nanotube-cluster assemblies for chemical sensors. Our dynamical simulations of Li diffusion show that Li ions are highly mobile inside carbon nanotube ropes and do not exhibit correlated motion even at fairly high concentrations, indicating the suitability of nanotube/Li materials for very high capacity batteries. Turning to pyroelectric effects, we have shown that most BN nanotubes exhibit a large, built-in electric field along the nanotube axis, as well as large piezoelectric coefficients. Our results show that BN nanotubes will be excellent components of nanotube-based nano-electro-mechanical systems (NEMS), including actuators, switches, and transducers. The spontaneous electric field also induces interesting effects in BN/C structures, where significant lowering of the work function can be accomplished by a suitable arrangement of BN/C junctions, leading to substantially enhanced electron emission. Nanotubes are also excellent candidates for components of nanoscale electronic devices. Our research shows that some nanotubes can act as nanoscale strain sensors, while others are flexible ballistic conductors. Their properties can be exploited in single electron transistors, spintronic devices, and even nanoscale chemical sensors with single-molecule sensitivity.

Introduction

There is currently considerable amount of scientific interest in the emerging field of nanotechnology, largely because of anticipated future technological gains. Perhaps no other material has contributed more towards our understanding of this field than carbon nanotubes [1]. Carbon nanotubes, which have been shown to form spontaneously in a variety of growth conditions, are built up of cylindrical graphitic sheets where three-fold coordinated carbon atoms connect seamlessly to each other. They are now known to have unique mechanical and electronic properties. Indeed, because of the strength of the grapheme sp^2 bond, carbon nanotubes may well be Nature's ultimate-strength fibers which should enable future high

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strength/low weight applications. Clearly, if such materials can be fabricated cost effectively and in bulk, many important space applications will become possible. Aside from their exciting mechanical properties, nanotubes have considerable future as sensors and energy storage devices [1]. Carbon nanotubes may be either metals or semiconductors, so that an all-carbon nanotube based electronic system may be formed at the nanometer length scale. Nanotube-based sensors take advantage of the fact that the electronic properties of the nanotubes change, depending on the materials that contact the tubes.

In this paper, we review some of our recent theoretical investigations of carbon nanotubes and related materials [2-6]. Our investigations are based on a combination of large-scale quantum and classical molecular dynamics simulations. Specifically, we have focused on issues related to the strength of nanotubes [2], their ability to act as energy storage devices [3], and the enhanced field emission properties of boron nitride/carbon nanotubes (BN/C) [4]. We have also investigated the quantum transport properties of various nanotube configurations, including the conductance signatures of pristine and defective nanotubes, their dynamical response, nanotube-based magnetic tunnel junctions, and nanotube-based sensors [5,6]. The results show that nanotubes are suitable for a number of breakthrough applications in the context of space exploration as well as earth-bound systems.

Mechanical Properties of Nanotubes

As already noted, nanotubes can be viewed as “rolled-up” grapheme sheets and because graphite is exceptionally strong with respect to in-plane deformations, nanotubes possess extraordinary mechanical properties. Moreover, nanotubes are relatively light – approximately one sixth the weight of steel – which should lead to a variety of future applications as a superstrong material. Our work on the mechanical properties of nanotubes [2] has focused primarily on two aspects: the elastic deformations where the shape of the nanotubes may change but the local atomic coordination does not, and the onset of irreversible changes where the atomic structure changes. In all cases, nanotubes were shown to be exceptionally elastic and strong: they can reversibly bend to very high angles, and their tensile strength is unmatched by any known material.

Since the breaking and reforming of bonds at large strains is inherently a microscopic process, detailed atomistic simulations are necessary in order to determine the limits of nanotube strength. These simulations – of both a quantum and classical nature – show that beyond a critical value of the tension, the system releases its excess strain via a spontaneous formation of topological defects. The first defect to form corresponds to a 90° rotation of a C-C bond about its center, the so-called Stone-Wales transformation [7], which produces two pentagon-heptagon pairs as shown in Fig. 1. Static calculations under fixed dilation show a crossover in the stability of this defect configuration with respect to the ideal hexagonal network. The crossover was computed to occur at about 6% tensile strain in (5,5) and (10,10) armchair nanotubes [2]. Subsequent experiments [8] have indeed found that nanotubes fail at strains of up to a little over 5%. Since both theoretical calculations and experiments measuring the Young’s modulus of graphite give an exceptionally high value of over 1 TPa, nanotubes are the strongest materials known. Indeed, a direct measurement of breakage strengths of nanotube ropes gave values ranging up to 52 GPa.

The knowledge of the dominant strain-release mechanism enables investigations of both the thermodynamic limit of nanotube strength and of kinetic effects. While the armchair nanotubes are thermodynamically stable up to strains of 6%, for zigzag nanotubes the crossover in stability occurs at 12-14%, indicating truly enormous strength. Up to these strain values, the nanotubes will deform elastically. Beyond this,

the response depends on the kinetic barrier. Our computed activation energy for the bond rotation is of the order of 6-10 eV, depending on the strain. Given the large magnitude of this activation energy, the nanotube will deform elastically in a much greater strain regime. The variation of stability with respect to the helicity (e.g., armchair vs. zigzag) may be understood by examining the limiting cases. When strain is applied to an armchair nanotube, the rotating bond is originally perpendicular to the strain axis and becomes parallel when the defect is formed. The result is a slight release of the strain. In (n,0) zigzag nanotubes, however, the rotating bond forms a 120° angle with respect to the strain axis, so that after the rotation there is no obvious gain in terms of strain release. Curvature effects modify this argument somewhat, but it predominantly remains valid.

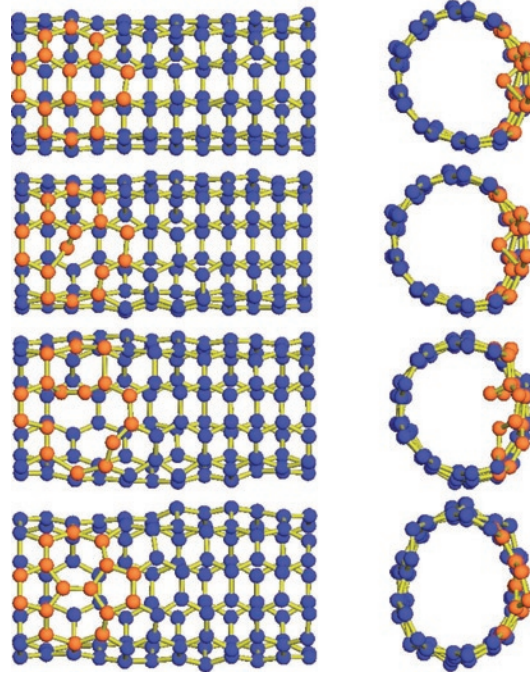


Fig. 1. Quantum molecular dynamics simulations show that nanotubes initiate breakage by a bond rotation, where a pair of atoms rotates about the center of their bond and converts four hexagons (highlighted in red) into a 5-7-7-5 defect. The barrier for this rotation is very high, which further increases the exceptional strength of nanotubes.

Viewed in the context of our results, the 52 GPa experimental value appears to be a significant underestimate, because the activation energies are very high and the measurements are performed at room temperature. Indeed, a simple estimate based on the Arrhenius expression, $\Gamma \sim N_{\text{bonds}} \nu \exp(-E_{\text{act}}/k_B T)$ with $\nu \sim 10^{13}$, gives a negligible rate of defect formation at room temperature. Since perfect nanotubes should be much stronger, it is likely that the nanotube samples used in these experiments contained defects. This is consistent with the relatively poor quality of nanotubes produced by current growth techniques. As the quality of growth and processing increases, the maximum strength of nanotube bundles should be much increased.

The defect formation and propagation in strained nanotubes has an interesting geometrical interpretation. The appearance of a (5-7-7-5) defect can be viewed as the nucleation of a degenerate dislocation loop in the planar hexagonal network of a grapheme sheet. The (5-7) defect behaves as a single-edge dislocation in the graphitic plane. Once formed, the (5-7-7-5) dislocation loop can ease further relaxation by separating

the two dislocation cores, which glide through successive bond rotations. This corresponds to a plastic flow of dislocations and gives rise to ductile behavior. Alternatively, larger defects may also be nucleated from the (5-7-7-5) defect, leading to crack extension. It is also important to note that the plastic flow of defects changes the helicity indices of the nanotubes, potentially leading to metal-semiconductor junctions that could be used to fabricate novel nanoscale devices.

Li Storage in Nanotube Ropes

Recent developments in secondary Li-ion battery technology have focused on replacing metallic Li electrodes with Li-carbon guest-host compounds in order to enhance both safety and cyclability concerns. In Li-carbon systems, the use of a solid electrode host prevents the reduction of Li ions to dangerous levels of metallic Li during the charge-discharge process [9]. This is the main reason why current rechargeable battery technology is dominated by graphitic carbon anodes. However, the use of graphite as a host material has a practical tradeoff in the reduction of the energy density, when compared to that of the metallic system. This drawback is chiefly due to the limited Li uptake in graphite. At best, the Li/C ratio for graphite is 1:6. In terms of battery power, this implies a reduction of the specific capacity of the anode from 3860 mAh/g for metallic Li to 372 mAh/g for Li-graphite intercalation systems.

Thanks to their unique structure, it is believed that carbon nanotubes can provide a good alternative for improving the Li ion capacity. Typically, the nanotubes arrange themselves into “nanotube ropes” consisting of a large number of nanotubes situated on a hexagonal lattice, all held together by van der Waals interactions [1]. For intercalation, nanotube ropes therefore have two potential channels open for Li uptake: the interstitial channels between the individual nanotubes in the ropes, and the nanotube interiors – provided that the latter region is accessible to the ions. Theoretically, if both of these channel are open it would dramatically increase the Li/C ratio to 1:2, thereby increasing the energy density of the battery to 1118 mAh/g [10].

Since Li intercalates readily into the channels between nanotubes, the key for enhanced Li uptake in nanotube systems lies in the ability of ions to move in and out of nanotube interiors at a reasonable rate. To address this issue, we have calculated the typical diffusion barriers encountered by the Li ions with *ab initio* simulations [3]. Our salient results are as follows. First, it is difficult for Li ions to enter the nanotube interiors through the sidewalls of pristine nanotubes: the barriers here are very large, ~ 13.5 eV. It is therefore virtually impossible for Li to enter the nanotube interior via the direct diffusion through the sidewalls. Hence, other diffusion pathways must be found. One such option is provided by the various topological defects that can be induced in the nanotube sidewalls by nonequilibrium means, such as ion bombardment, tensile straining of nanotubes, or by the more violent means such as a chemical attack or direct mechanical grinding of nanotubes. Since all of the various topological defects consist of n -membered rings in various combinations, we have calculated the diffusion barriers for Li ions moving through such rings ranging from hexagons to decagons. As expected, as the number of sides n increases, the barriers for Li to enter decrease, because the “holes” get larger and larger. For an enneagon (9 sides) the diffusion barrier is already 0.5 eV, which can be easily surmounted at room temperature, while for a decagonal (10 sides) virtually no barrier separates the exterior from the interior. Barriers for smaller-sized rings are considerably larger. Hence, very large-sized defects are required for ions to enter nanotube interiors.

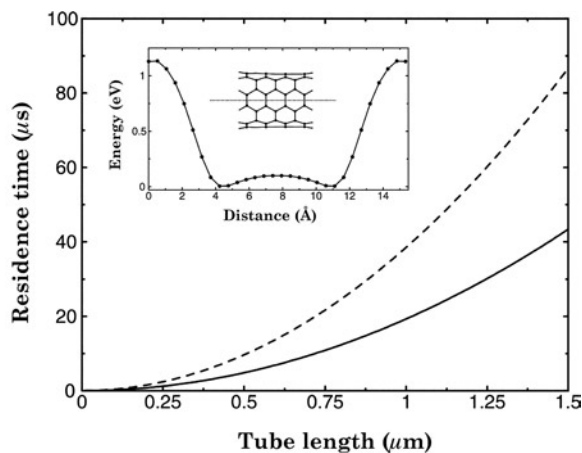


Fig. 2. Estimated residence time as a function of nanotube length $T=300$ K for Li atoms in either the nanotube interior (solid line) or interstitial rope channel (dotted line). The inset shows the energetics of a typical diffusion path calculated for Li moving through an open nanotube.

An alternate way for ions to enter is via open-ended carbon nanotubes. Such a pathway implies that the open ends of the nanotubes are stabilized by, e.g., hydrogen passivation. In this case, our investigations show that if the nanotubes are not too long (i.e., of the order of a few hundreds of nanometers), the movement of ions is not diffusion limited and Li can move in and out of the nanotube interiors with relative ease. Hence, the ideal nanotube configuration for battery applications consist of relatively short, open-ended nanotube ropes. These theoretical results are completely consistent with current experiments [11]. While initial experiments showed only a disappointing 25% increase in the reversible Li uptake, more recent experiments have shown that an aggressive ball-milling treatment and mechanical grinding, which both induce defects and shorten the nanotubes, leads to a much enhanced Li:C ratio of 2.7:1.

Field Emission from BN/C Nanotube Superlattices

BN nanotubes are a material related to carbon nanotubes insofar as they have a very similar structure. They have recently been produced in gram quantities, and are able to couple seamlessly to different carbon nanotubes [12]. This is exciting, because it opens up the possibility of forming different classes of nanoscale heterojunctions. Very recently, BN nanotubes have been predicted to possess a nonzero spontaneous polarization field, much stronger than those found in wurtzite semiconductors. Here, we report on a study of BN/C superlattices and heterojunctions that shows, by explicit calculations, that the spontaneous polarization fields present in BN/C systems could dramatically enhance the field emission properties of these composite nanotubes [4].

The presence of a spontaneous polarization field in BN/C nanotubes is a direct consequence of the polar nature of the B-N bond and the low symmetry of the underlying lattice. It is also clear that the symmetry of the nanotube plays an important role in determining the magnitude of the spontaneous polarization field. The strongest effects will be observed for the (n,0) zigzag tubes, since this geometry maximizes the dipole moment of the B-N bond. By contrast, (n,n) armchair tubes are not expected to display any spontaneous polarization field because any individual nanotube ring will be charge neutral, so that no extra fields are possible. We have shown by direct calculations that for zigzag BN/C nanotubes with helicity index $n=3l+1$ (l integer) the polarization field is significantly lower than for the other tubes. This effect

originates from the fact that the carbon sections – located between the BN ones – will most effectively screen the macroscopic polarization field. As shown in Fig. 3, the valence state is always localized within the carbon section. This state will display either a longitudinal or transverse symmetry, as exemplified by the (7,0) and (8,0) tubes, respectively. For $3l+1$ tubes, the valence state always assumes a longitudinal character, which enhances the magnitude of the depolarization field that is opposite to the one intrinsic to the BN section. In turn, this reduces the overall polarization in the BN/C superlattice, especially for the case of small-diameter tubes.

Despite the screening by the valence electrons distributed over the carbon portion of the BN/C superlattices, a net polarization field is built up along any zigzag structure. The existence of the intrinsic macroscopic field will clearly influence the extraction of electrons from these systems. Qualitatively, a good electron emitter is characterized by a large geometrical enhancement factor β and a small work function ϕ , which is an intrinsic property of the emitter material [13]. For nanotube systems, it is well known that the field enhancement factor increases linearly with size of the nanotubes, so that large enhancement factors are clearly possible for very long tubes [14]. In fact, the already desirable emitter properties of nanotubes may be further enhanced by adding BN near the tip. The idea here is to make use of the polarization fields in order to reduce the work function of the tips, thereby enhancing the extraction of electrons from the system.

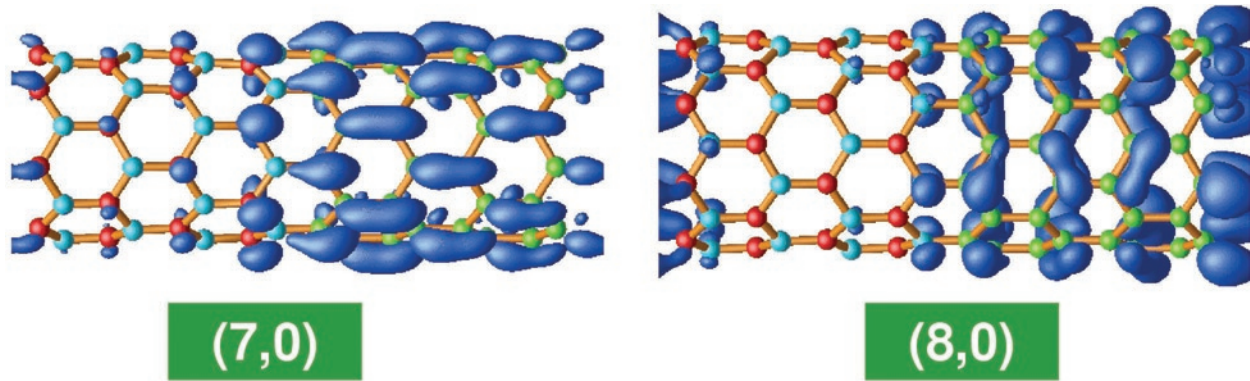


Fig. 3. Electron distribution in the top valence state for (7,0) and (8,0) BN/C nanotubes. Note that the symmetries of the two states are quite different.

In order to examine this effect quantitatively [4], we have built up (6,0) zigzag structures using B, N, and C in various combinations. The work functions were then computed as the difference between the vacuum level and the Fermi energy of the system. Our calculated values for work functions for carbon nanotubes are 5.01 eV for a (10,10) tubes, and 6.44 eV for the smaller diameter (6,0) nanotubes, in agreement with previously published results [15]. Turning to the heterostructures, the net polarization field experienced by the electrons reduced the work function to 5.04 eV for C-tipped structures and increases it to 7.52 eV for N-tipped tubes. For BN/C systems, the work function of the B tip takes on a value of 5.00 eV and 6.45 eV at the C tip. The work function is therefore decreased by a significant 1.40 eV, as compared to pure carbon systems. This is large enough to lead to significant macroscopic effects. According to the Fowler-Nordheim relationship [13], the logarithm of the current density (J) depends on the work function ϕ as $(\ln J) \sim \phi^{3/2}$. It follows that the insertion of BN segments in carbon nanotubes will increase the current density by up to two orders of magnitude as compared to pure carbon nanotube systems.

Electronic Properties of Nanotubes and Nanotube-Based Devices

Carbon nanotubes may be either metals or semiconductors [1], which opens up the exciting possibility of forming carbon nanotube-based devices and sensors. Indeed, with the aid of nanomanipulators, prototypical devices have already been formed, and their transport properties explored. Our work [5,6] has primarily been focused on understanding the transport properties of such devices – especially for the case of hybrid device structures in which nanotubes are electrically contacted to other materials.

At nanometer distances, electrons can move ballistically through a device without any scattering. For such structures, the current (I) and voltage (V) are related via $I=GV$, where G is the quantum conductance. In turn, the famous Landauer formula relates G to the transmission coefficient T via $G = (e^2/h) T$ [16]. In order to investigate transport through nanotube systems and calculate the transmission coefficients, we have constructed a simple and efficient procedure based on transfer matrices and the appropriate Green's functions [5]. For instance, metallic armchair nanotubes have two extended electron bands crossing at the Fermi level. Such nanotubes therefore behave as a two-channel ballistic conductor with a theoretical conductance of $G = 2G_0 \sim 2(12.9K\Omega)^{-1}$. In principle, at larger electron energies, the electrons are able to probe additional sub-bands which leads to a corresponding increase in G .

From our exploration of the mechanical properties of nanotubes, it has become clear that there is a strong coupling between the structural and electronic properties of nanotubes. For instance, experiments [17] have shown that individual carbon nanotubes deposited on a series of protruding electrodes could be classified into three groups depending on their electrical behavior: (i) non-conducting tubes at room temperature and below; (ii) conducting tubes at all temperatures; and (iii) partially conducting tubes. The last class represents nanotubes that are conducting at high temperatures, but at low temperatures behave as a series of quantum wires connected in series. It has been argued that local barriers in the wires arise from the bending of tubes near the edges of the electrodes. Loss of conductance was also observed when single-wall nanotubes are severely deformed by an AFM tip [18], and in the final stages of breakage of a multiwalled nanotube.

Motivated by these experiments, the PIs investigated theoretically the quantum conductance of bent nanotubes of both infinite [5] and finite sizes [6]. In general, the calculations show that the conductance of armchair nanotubes is relatively insensitive towards deformations: very large distortions are required before there is any substantial change in G . For chiral nanotubes, however, the local strain at a kink site opens up a small gap in the electronic spectrum. This extreme sensitivity can be exploited in switches and strain sensors. For nanotubes of finite lengths, the conductances consist of closely spaced peaks corresponding to the discrete energy levels of the finite system, which merge into the continuum limit as the length of the nanotube segments is increased. The distribution of these peaks is length dependent, and may be understood in terms of the band structure of tubes. With these theoretical considerations, the PIs have tentatively interpreted the three classes of transport behavior as being due to (i) semiconducting, (ii) armchair and (iii) chiral nanotubes. The interruption in conductance upon severe bending can also be used in device design. For example, by kinking a nanotube in two nearby locations a small quantum dot can be produced, which forms the heart of a single electron transistor that operates at room temperature [18].

Critical to the operation of any nanotube-based device is the issue of constructing good metal to nanotube contacts. As already mentioned, ideal nanotube-metal devices should have a contact resistance in the $k\Omega$ range. While the ideal resistance has recently been achieved [19], most nanotube-based devices display

resistances in the $M\Omega$ range. What is the physical origin behind the very high contact resistance of nanotube systems? As a prototypical example, we have considered the transport properties of metallic (5,5) nanotubes deposited on an Al(111) surface with accurate self-consistent *ab initio* calculations [20], in order to properly account for any potential charge transfer between the two very dissimilar materials. As shown in Fig. 4, there is some reduction in G when the tube is placed on the metal. However, the magnitude of G remains substantial. More insight may be obtained by plotting the eigenchannels for the transmission, which separate into two separate entities localized on either the metal or the nanotube, respectively. Since there is very little hybridization and intermixing between the nanotube and the metal, the electron transfer between the nanotube and metal is very inefficient. This weakly distributed coupling may explain the high nanotube-metal contact resistance observed experimentally. On a related issue, if the contacts to a finite-sized nanotube are highly resistive, the nanotube can behave as an effective quantum dot, with conductances exhibiting Coulomb blockade behavior. One feature of Coulomb blockade physics observed in nanotubes is that the conductance peaks are higher and lower depending on whether the number of electrons in the carbon nanotube is even or odd [21]. This low-to-high peak alternation continues as a function of the applied gate voltage, and with a saturation current that is nonsymmetric with respect to the polarity of the bias voltage. We have shown that these interesting results may be understood in terms of the spin-degenerate levels in the dot that are split when occupied by an electron repulsion energy [6].

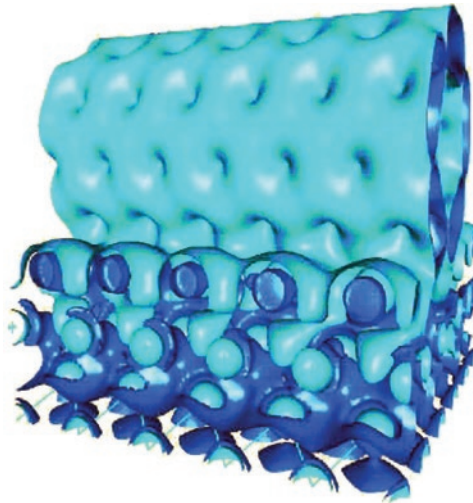


Fig. 4. Electron distribution across a nanotube-aluminum contact.

Hybrid junctions in which carbon nanotubes are contacted electrically to materials with more exotic characteristics have recently been the focus of several experiments. For instance, spin-coherent transport in a carbon nanotube magnetic tunnel junction was recently investigated experimentally by attaching two cobalt leads to a nanotube [22]. The PIs have investigated such junctions theoretically after suitably generalizing their transport code in order to account for spin effects, and observed clear signatures of a spin-valve effect as shown in Fig. 5 [6]. Briefly, coupling the nanotube to ferromagnetic leads allows for spin-polarized electrons to be injected into the nanotube device. When the magnetizations of the two leads are parallel, the electrons can move freely through the device and the resistance is low; when they are antiparallel, there will be considerable scattering of the electrons at one of the interfaces, which leads to a relatively high resistance. Hence, it is possible to construct magnetic tunnel junctions and other spintronic devices at the nanoscale level using nanotubes, in analogy with more conventional magnetic technology.

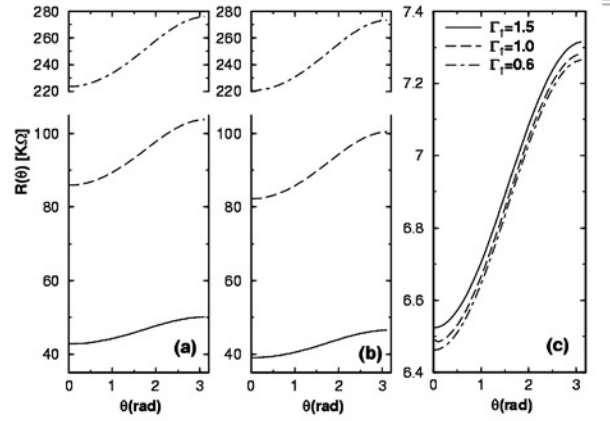


Fig. 5. Resistance of a (5,5) carbon nanotube device for different coupling parameters and tube lengths as a function of angle θ - the angle between the magnetization of the left and right-leads, respectively. Here, (a) length 5 units; (b) length 6 units; and (c) length 7 units, for different values of couplings. Note the characteristic signatures of a spin valve effect - low resistance when $\theta=0^\circ$ and high resistance when $\theta=180^\circ$. Also note that while the same characteristic behavior is obtained for all the devices, the magnitude of the effect is length dependent, reflecting the band structure of the nanotubes [6].

Most interestingly, there have been recent experimental studies of nanotubes coupled to superconducting niobium leads [23]. By tuning the transparency of the device with a gate voltage, clear signals of Andreev reflections were detected via changes in the sub-gap resistance, while an additional narrow peak in the dV/dI curves emerged at $T=2K$. While Andreev reflections, in which an electron propagating from the normal metal side of a metal-superconducting junction is converted into a Cooper pair and a backscattered hole, are well known, the emergence of an additional low-temperature peak has originally been viewed as a characteristic of a correlated many-body Luttinger liquid. However, a single-electron-based theoretical analysis for the nanotube-superconducting system is in good semiquantitative agreement with the experimental results. Even more satisfying is that at very low temperatures a narrow peak emerges from the calculations, which are solely based on single-electron effects without the inclusion of any many-body effects whatsoever. A simplified analysis identifies its origin as being due to a small splitting between the electron and hole levels that occurs when the nanotube is contacted to the superconducting lead. This leads to the formation of a small peak in the differential conductance, which is washed out as the temperature is increased.

So far all of the aspects of quantum transport considered here are based on the flow of direct (DC) currents through nanotube systems. What about the flow of alternating currents (AC)? AC conductance in material systems is complicated by the presence of time-dependent fields that can take the system out of equilibrium. Under AC conditions, electrodynamics shows that displacement currents are induced, which need to be accounted for if the total current is to be conserved and gauge invariance maintained. Another important feature associated with AC response is that of photon-assisted tunneling. In the presence of a time-varying potential, electrons can absorb photons and thereby inelastically tunnel through higher energy levels [24].

We have investigated the dynamic response of carbon nanotubes in the wideband limit [6]. In general, dynamic effects are quite small for low AC frequencies. For larger frequencies in the 0.1 to 1 eV range,

there is a general reduction in the conductance because the displacement currents act to reduce the normal conduction current. At higher frequencies, the trend is actually reversed and the conduction is actually increased. This effect is due to photon-assisted tunneling, which places the electrons into the higher energy subbands. The net result is that conductance, after an initial decrease, is greatly enhanced. In the presence of a time-varying electric field, the conductance is characterized by the emergence of an imaginary component which signals that the nanotubes acquire both a capacitive and/or inductive behavior depending on the frequency. We also note that the AC frequencies to which the nanotubes respond are well in the infrared to optical range, and hence it should be useful to explore future nanotube-based optoelectronic devices when combined with semiconductor technology.

As the last application, we describe work towards developing nanosensors with well-defined sensitivity towards specific reagents. Our initial project involves investigations of nanotube-cluster assemblies. In our exploratory work, we have already shown that Al_{13} clusters adsorbed on nanotubes act as molecular sensors, and are sensitive towards the adsorption of a single ammonia molecule, whose adsorption can be electrically detected. The atomic configuration of the sensor structure is shown in Fig. 6. Future work will explore other metals, which do not oxidize easily, and the attachment of receptors, so that the sensor will be sensitive only towards specific reagents.

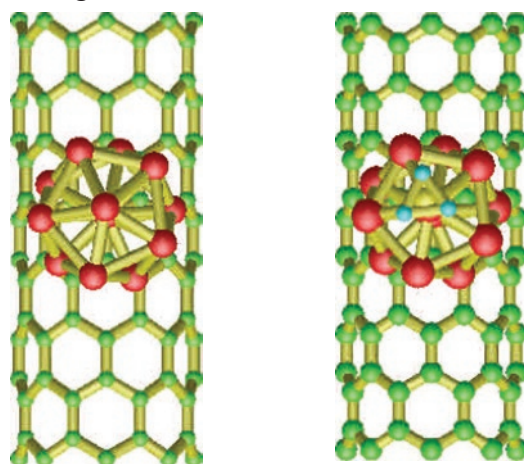


Fig. 6. An Al_{13} cluster attached to a nanotube can serve as a chemical sensor. The originally semiconducting nanotube becomes conducting when an ammonia molecule is attached to the cluster. The figure shows the atomic configuration before and after the attachment.

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DISPERSION MICROSTRUCTURE AND RHEOLOGY IN CERAMICS PROCESSING

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Ceramics provide a potentially very useful class of materials owing to their physical properties; they are light, hard, resistant to abrasion, chemically inert, stable at high temperatures, and excellent thermal and electrical insulators. Further, by casting from a liquid suspension and subsequently sintering, many complex parts and shapes can be fabricated. Although the resultant properties of ceramics can be outstanding, they often suffer from extreme brittleness, caused by the propagation of cracks, which is in turn due to microstructural defects. These defects may be caused by a number of different factors, such as particle agglomeration, migration or segregation prior to sintering, or due to inhomogeneous volume change upon sintering.

Typically, high-performance ceramics are produced using monodisperse micron-sized particulate suspensions from which the ceramics are cast. By controlling the size and processing, a dense uniform microstructure may be formed prior to sintering. This route has met with limited success even though the maximum volume fraction of ceramic particulates that can be achieved prior to sintering is 0.74. The limited success may stem from the fact that a perfect crystal of mono-sized particles has slip planes that yield easily, and from the fact that there is still a large amount of void space that must be eliminated upon sintering.

An alternate approach is to use a mixture of particle sizes. It is well known that solids fractions of 90% can be obtained with a bidisperse suspension of spherical particles. Crystalline slip planes can be eliminated with a mixture of particle sizes. In addition to achieving high solids fractions, and therefore reducing potential sintering inhomogeneities, a mixture of two different types of particles can also impart desirable properties in a ‘composite’ ceramic. Owing to size or compositional differences, particle mixtures are subject to gravitational phase separation or demixing, which can severely limit the utility of these systems. Thus, processing in microgravity may provide an attractive environment for producing advanced ceramics.

We have developed a new $O(N \ln N)$ simulation method with full hydrodynamics – Accelerated Stokesian Dynamics – to study the microstructure and determine the macroscopic properties of colloidal dispersions used in ceramics processing. Results are obtained for the shear and normal stresses, particle diffusivities and the shear-induced microstructure.

Keywords: ceramics, Stokesian Dynamics, computer simulation, new research

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OPTICAL ELLIPSOMETRY AND X-RAY SCATTERING FOR CHARACTERIZING ORDER IN LIQUID CRYSTALLINE POLYMERS AND BIOPOLYMERS

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We report results of optical and wide and small angle X-ray scattering studies of structure development in collagen-model peptides. Our custom built two-dimensional optical ellipsometer is used to provide retardance and azimuthal angle information about the state of order in optically anisotropic structures. Recently, we have applied this instrumentation to investigate biological molecules, viz., oligomeric peptides with amino acid structures that are models for collagen. Proline and hydroxyproline residues stabilize the triple-helical conformation of collagen proteins in the collagen consensus sequence. Regular modifications have been introduced into the collagen consensus sequence, forming model systems for the study of bio-macromolecular organization. The model systems are oligomers with hexapeptide sequences of the form: $(\text{Glu})_5(\text{Gly-Ala-Pro-Gly-Pro-Pro})_6(\text{Glu})_5$ or $(\text{Glu})_5(\text{Gly-Pro-Ala-Gly-Pro-Pro})_6(\text{Glu})_5$. The glutamic acid capping the ends of the hexapeptide sequences imparts solubility in water. Depending upon concentration and temperature, the peptides form lyotropic liquid crystalline structures, and maintain their order when dried to powders suitable for X-ray studies. Through the use of the high intensity source of X-radiation at the Brookhaven National Synchrotron Light Source, phase transformation kinetics and structure development are studied *in-situ*, providing time-resolved characterization of these peptides. Coupled with the optical imaging ellipsometry, these approaches provide the most complete information about microstructure in these systems. The goal of our research is to evaluate the ability of these model peptides for self-assembly into liquid crystalline and true three-dimensional crystalline phases and to assess the temperature stability of resultant higher order structures.

Keywords: optical ellipsometry, x-ray scattering, liquid crystals, polymers, biopolymers

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STEP BUNCH EVOLUTION ON VICINAL FACES OF KDP

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For in-situ studies of the formation and evolution of step patterns in solution growth, we have assembled an experimental setup based on Michelson interferometry with the growing crystal surface as one of the reflective surfaces. The device allows data collection over a relatively large area (approximately 4 sq. mm) in situ and in real time during growth. The depth resolution is improved over traditional interferometry using phase-shifted images combining by a suitable algorithm. We achieve a depth resolution of approximately 50 Angstroms. Lateral resolution, dependent on the degree of magnification, is around 0.3 to 5 microns.

The crystal chosen as a model in this work is potassium dihydrogen phosphate (KDP), the optically non-linear material widely used in frequency doubling applications. Kinetics of KDP crystallization is well studied so that KDP can serve as a benchmark for our investigations. We present quantitative results on the onset, initial stages and development of instabilities in moving step trains on vicinal crystal surfaces at varying supersaturation, flow rate, and flow direction. The kinetics data suggest that at low supersaturations, step bunching is caused by impurity retardation of the steps, while at higher supersaturations, we link the non-linearity during growth to interdependence of the velocity and density of the steps evidenced in independent experiments. The behavior on the surface is very dynamic, small bunches both merge and split from larger bunches as they travel across the facet. We present evidence that despite these dynamics, under steady conditions there exists a limiting value to step bunch height. This height is reached at distances between 600 and 1000 μm from the step source. In our experiments, we observed the retention of this step bunch height limit up to the path of 1500 μm .

Keywords: solution growth, stability, steps, KDP, interferometry

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FORCES DURING MANUFACTURE AND ASSEMBLY OF MICRO-SCALE DISCRETE ELECTRONIC COMPONENTS

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Micron scale manufacturing is becoming increasingly important as the use of portable electronic devices grows. Integration of discrete, micron scale components into portable electronic devices, increased use of microelectromechanical systems, and scaling down of combinatorial approaches for materials development are driving a need for novel microscale assembly methods and a better fundamental understanding of forces on microscale objects. Our objective in this research was to explore the forces on micron scale objects during assembly processes. Our approach was to use controlled electric fields to manipulate micron scale objects. An apparatus for manipulating micron-scale dry dielectric materials has been developed and used to collect and deposit polystyrene and silica spheres. A surface charge measurement device and finite element calculations have been used to quantify electrostatic forces on these particles. This technique not only provides insight into the forces on micron scale objects, but has direct application as a revolutionary rapid dry powder dispensing technique, which will increase the palette of materials available for exploration by high throughput combinatorial methods. A similar electric field technique has been used to manipulate micron scale silica particles in an aqueous medium. Metal microelectrodes were prepared by lithographic patterning. Particle motion was imaged in real time using an inverted metallurgical microscope focused on the plane containing the particles. Particles were observed to pack at the electrodes in the presence of an applied DC field. This particle motion was characterized as a function of field strength, pH, and ionic strength of the background electrolyte. AC fields were also employed in an attempt to reduce the polarization of the particles and electrodes. A particle chaining process is reported during which particles aggregate in single lines parallel to the applied AC field. Particles were also seen to adhere to the sapphire substrate near the electrodes during application of the field. A technique for tracking the two dimensional stochastic motion of particles settled on the substrate was developed and used to characterize the adhesion as a function of pH and ionic strength. Electrokinetic measurements for the particles and substrate were used as inputs to a dissimilar surface charge interaction model. The potential energy was calculated and used to explain the observed adhesion.

The use of an applied electric field to attract powder particles from a powder bed to a charged electrode above the powder bed surface may be used to study forces on micron scale forces in an electric field, and has been applied to the development of a novel dry powder dispensing system. The electrostatic dispensing apparatus is shown schematically in Figure 1. A surface charge measurement device was developed to measure any triboelectric surface charge that may have been deposited inadvertently on the surface of the powder bed in an effort to quantify Coulombic forces. This apparatus is shown schematically in Figure 2.

Keywords: electrophoretic forces, electrophoresis forces, high-throughput development, component assembly, particle motion, new research

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The surface-charge measurement device is used in a manner similar to an electrostatic force microscope. The conductive cantilever is electrically grounded, so that an image charge develops on the tip when it is brought near a charged surface. This results in an electrostatic force between the charged surface and the tip, and causes the tip to deflect toward the surface. The laser displacement meter is used to measure the deflection, which is proportional to the amount of charge on the surface. The deflection of the tip was calibrated by placing an electrode connected to a voltage source beneath the tip, and measuring the deflection as a function of applied voltage. The resulting data is shown in Figure 3. The curve indicates that a surface potential as small as approximately 50 V will result in a measurable deflection of the cantilever.

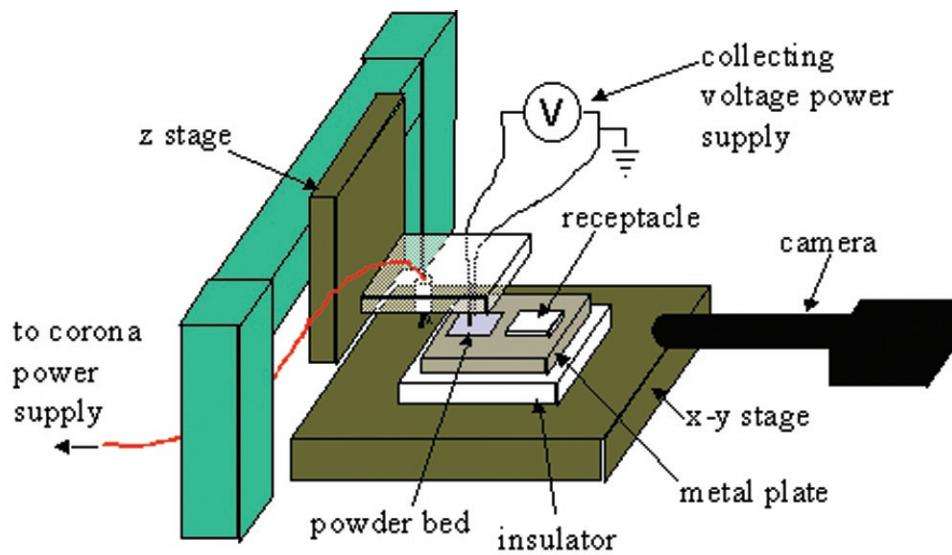


Figure 1: Electrostatic Microdispensing Apparatus

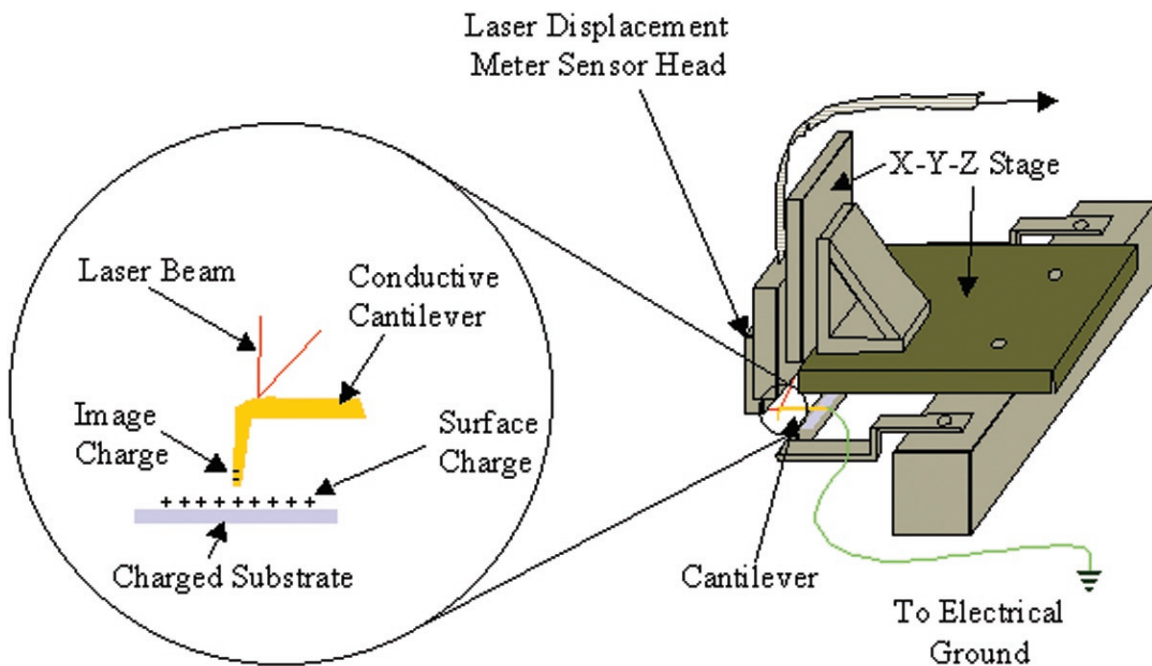


Figure 2: Surface Charge Measurement Apparatus

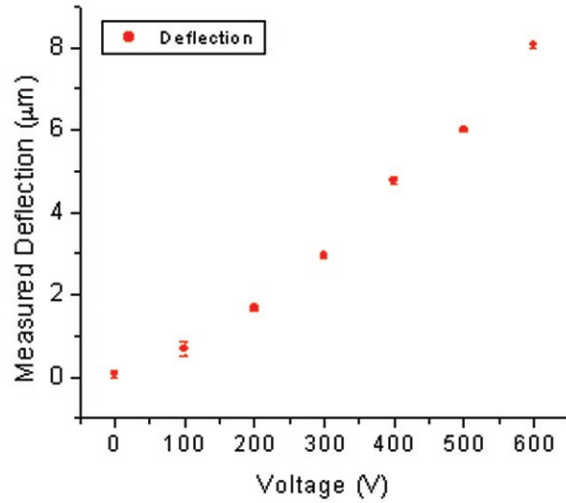


Figure 3: Calibration curve for surface charge measurement device.

The collecting voltage power source for the electrostatic microdispensing apparatus is used to apply an AC or DC electric field between the two collecting electrodes, or between a single collecting electrode and the metal plate containing the powder bed. The powder particles are attracted from the powder bed to the collecting electrodes upon application of the voltage. The applied voltage V , the separation between the electrodes and the powder bed, H , and the frequency of the applied field may be varied to control the amount of powder collected. Various electrode configurations have been used to dispense glass and polystyrene spheres. One configuration consisted of a cylindrical electrode terminated by a flat disc, placed above the powder bed. The electric field used to collect the spheres was applied between the cylindrical electrode and the metal plate beneath the powder bed. No surface charge was intentionally applied to the spheres prior to collection. Figure 4 below shows the spheres were attracted to the cylindrical electrode upon application of a positive DC voltage. Figure 5 shows the spheres attracted to the cylindrical electrode upon application of a negative DC voltage. Figure 6 shows the spheres attracted to the cylindrical electrode upon the application of an AC voltage.

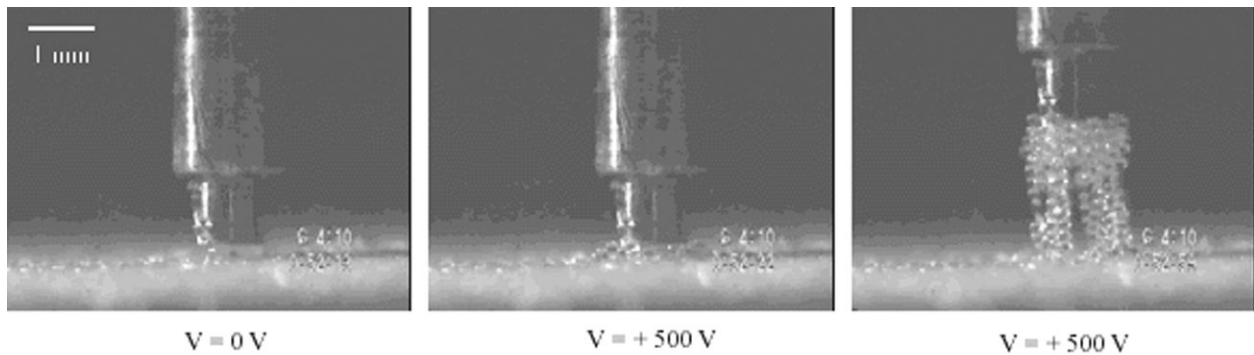


Figure 4: Collection of “uncharged” glass spheres upon application of a positive DC voltage to cylindrically shaped electrode. $V = +500 \text{ V}$, $H = 100 \text{ μm}$.

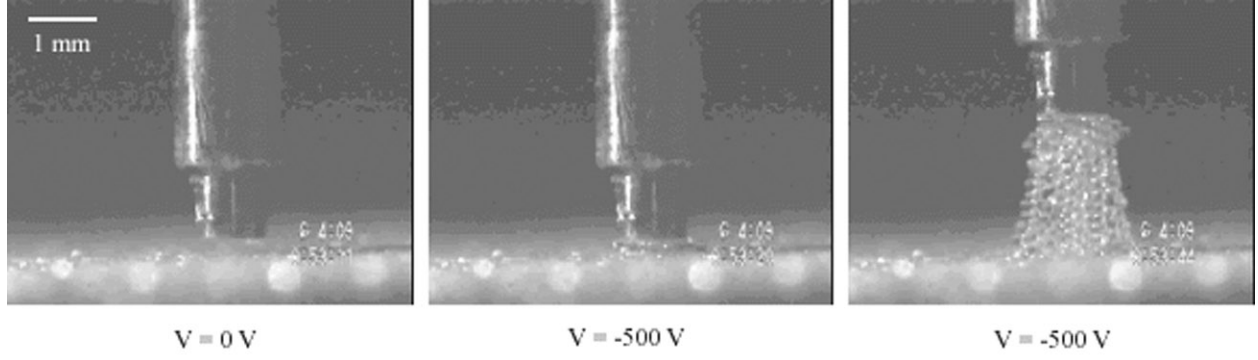


Figure 5: Collection of “uncharged” glass spheres upon application of a negative DC voltage to cylindrically shaped electrode. $V = -500$ V, $H = 100$ μm .

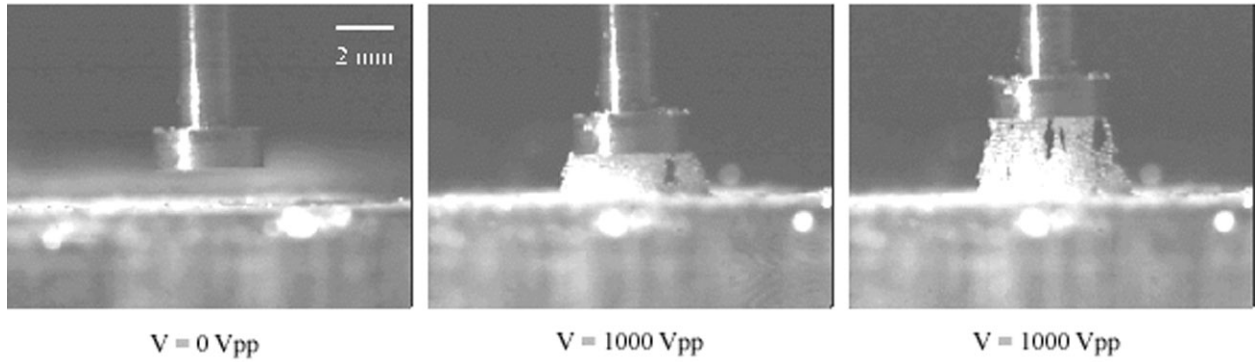


Figure 6: Collection of “uncharged” glass spheres upon application of an AC voltage to a cylindrically shaped electrode.

Although no surface charge was intentionally applied to the glass spheres, a small triboelectric charge may have been imparted to them during handling. Any surface charge present on the spheres will result in a Coulombic force upon application of an electrostatic potential between the collecting electrode and the grounded metal plate beneath the particles. The fact that the particles move towards the cylindrical electrode upon application of a positive, negative, or alternating potential suggests that forces other than a Coulombic force may be acting on them. The small, cylindrical disc-shaped electrode configuration generates a spatially non-uniform electric field, with a high electric field concentration around the lower edge of the disc. Dipoles induced in the dielectric particles interact with the electric field to produce a net dielectrophoretic force on the particles. The generalized multipolar dielectrophoretic force on a particle is given by equation 1, where a is the particle radius, $\vec{E}$ is the electric field, and ϵ_1 is the dielectric constant of the surrounding medium.¹

$$F_{DEP} = 2\pi\epsilon_1 a^3 K_1 [\vec{E} \cdot \nabla \vec{E}] + \frac{2}{3} \pi a^5 \epsilon_1 K_2 [\nabla \vec{E} : \nabla^2 \vec{E}] + \frac{1}{15} \pi a^7 \epsilon_1 K_3 [\nabla^2 \vec{E} : \nabla^3 \vec{E}] + \dots \quad (1)$$

The effective polarizability of a sphere, with permittivity ϵ_2 in a medium of permittivity ϵ_1 is given by the polarization coefficient K , shown in equation 2.¹

$$K_n = \frac{\epsilon_2 - \epsilon_1}{n\epsilon_2 + (n+1)\epsilon_1} \quad (2)$$

In order to quantify the forces acting on the spheres during collection, it is necessary to separate any Coulombic force from the dielectrophoretic force. The surface charge measurement device was used to measure the charge of the surface of the spheres. The laser displacement meter on the surface charge measurement apparatus is capable of registering a deflection of the cantilever resulting from a surface potential of approximately 50 V on a charged surface placed 0.01 inches below the cantilever tip. When placed above the powder bed surface, no deflection of the cantilever was measured. This indicates that the surface potential on the glass beads must be less than approximately 50 V. This is equivalent to a surface charge density of approximately $1.7 \times 10^{-7} \text{ C/m}^2$. Spheres were attracted from the powder bed using the electrode configuration shown in figures 1 and 2, at an applied voltage, V , of 300 V and a separation, H , of 350 μm . Near the center of the disc electrode, the electric field in the powder bed, E_2 , is approximately given by equation 3, where V_2 is the voltage drop across the powder bed and t is the thickness of the powder bed.

$$E_2 = \frac{V_2}{t} = \frac{V}{t + \epsilon_2 H} = 7.14 \times 10^4 \text{ V/m} \quad (3)$$

The resulting approximate Coulombic force on a single 150 μm glass sphere is 0.0088 μN , while the gravitational force acting on the sphere is 0.043 μN . This suggests that the dielectrophoretic force is dominant, and any Coulombic force is negligible.

An electrode configuration consisting of two concentric wire rings, shown schematically in Figure 7, has been used to investigate the effects of the magnitude and frequency of the applied voltage, V , and the initial separation, H , between the electrodes and the powder bed surface on the total amount of powder collected.

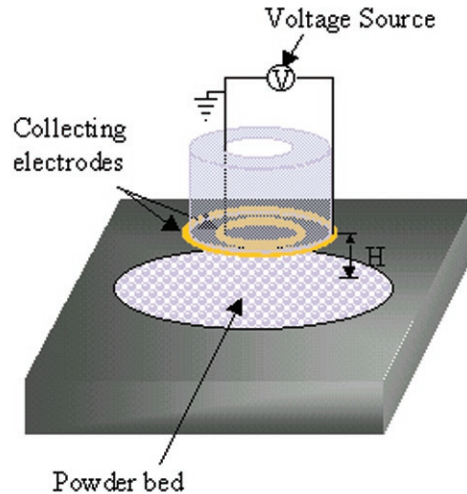


Figure 7: Concentric Rings Electrode Configuration

The electric field has been calculated for this axisymmetric electrode configuration using a commercial finite element software package from Algor, Inc. The model used is shown in Figure 8. The resulting electric field distribution for an applied voltage of 600 Vpp, at a frequency of 5000 Hz, and an initial separation of 0.1 mm using a powder bed made up of 100 μm polystyrene spheres is shown in Figure 9. The packing density of the powder bed has been graded from 30% at the powder bed surface to 60% in the bulk, over a distance of three particle diameters.

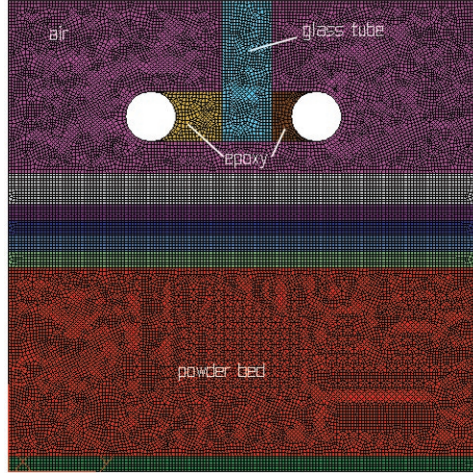


Figure 8: Finite element model for calculation of electric field distribution.

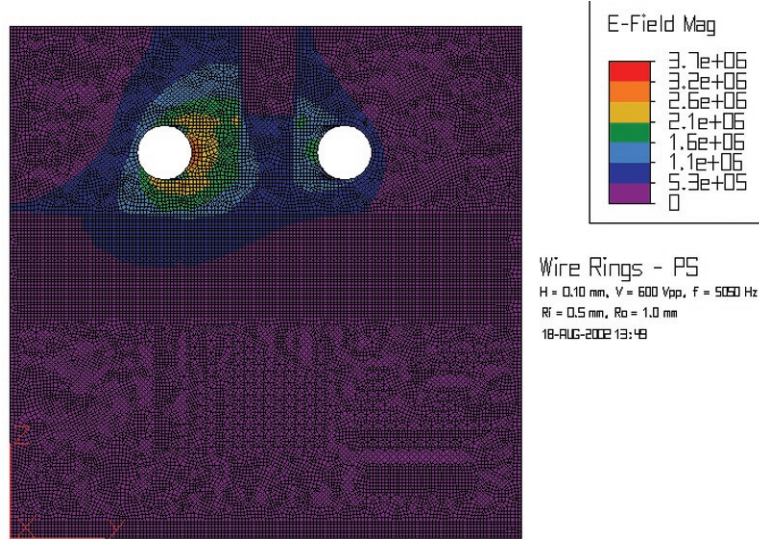


Figure 9: Calculated electric field distribution for model shown in figure 8. $V = 600$ Vpp, $H = 0.1$ mm, $f = 5000$ Hz for $100 \mu\text{m}$ polystyrene spheres.

The dielectrophoretic force on a homogeneous, lossless spherical particle is given by equation 1. For lossy dielectric particles and medium, the permittivities in equation 2 must be replaced by the complex permittivity, ϵ^* , given by equation 4, where ϵ is the dielectric constant, σ is the conductivity, and ω is the frequency of the applied electric field.

$$\epsilon^* = \epsilon + \frac{\sigma}{j\omega} \quad (4)$$

The resulting time-average dielectrophoretic force is given by equation 5, where $\text{Re}[K_n]$ is the real component of the complex polarization factor.

$$\langle F_{DEP} \rangle = 2\pi\epsilon_1 a^3 \text{Re}[K_1][\vec{E} \cdot \nabla \vec{E}] + \frac{2}{3}\pi a^5 \epsilon_1 \text{Re}[K_2][\nabla \vec{E} : \nabla^2 \vec{E}] + \frac{1}{15}\pi a^7 \epsilon_1 \text{Re}[K_3][\nabla^2 \vec{E} : \nabla^3 \vec{E}] \quad (5)$$

A Matlab algorithm has been developed that uses the calculated electric field input, and employs nested loops to calculate the numerical derivatives of the electric field, which in turn are used in equation 5 above

to calculate the total time-averaged dielectrophoretic force for an arbitrary electrode configuration.^{2,3} This technique has been adapted to the axisymmetric geometry shown in Figure 7. The calculation indicates that the dielectrophoretic force acts to draw the particles near the surface of the powder bed towards the concentric ring electrodes. The number of particles collected may be roughly estimated as those in regions where the initial vertical component of the dielectrophoretic force is larger than the sum of the gravitational and van der Waals adhesion forces acting on the particles. The vertical component of the dielectrophoretic force is plotted as a function of position in Figure 10 for an applied voltage, V , of 600 Vpp and an initial separation, H , of 0.1 mm. The sum of the gravitational force and the van der Waals adhesion force for 100 μm polystyrene spheres is approximately 8.13×10^{-9} N. The estimated number collected for these conditions is approximately 258 spheres. Figures 11-13 show the estimated number of spheres collected in comparison with the experimentally measured values for varying voltages, separations, and frequencies. It is interesting to note that observed trends are in accordance with the expected trends from the calculated dielectrophoretic force, and the estimated amount is within a factor of two of the measured amount. This is further evidence that dielectrophoresis is the dominant force acting on the particles, and suggests that these simple calculations may be used to estimate the amount of powder that may be collected.

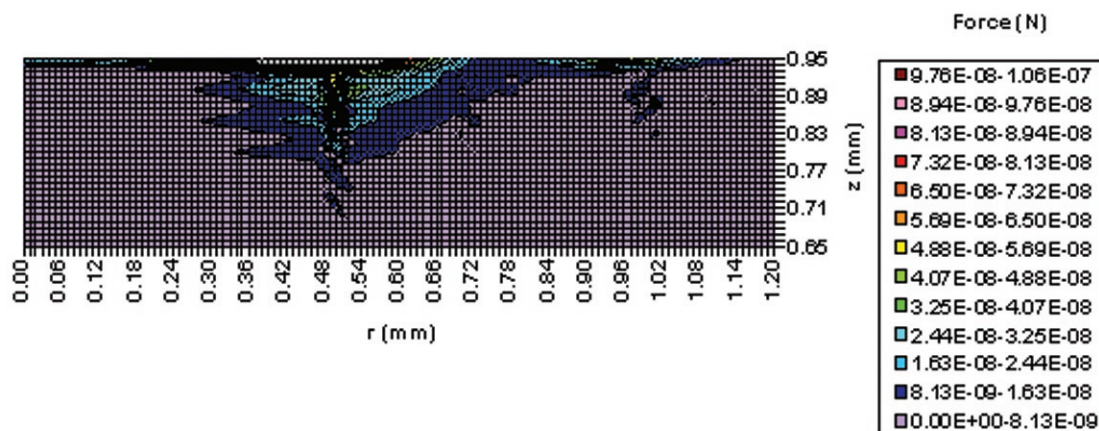


Figure 10: Vertical component of the dielectrophoretic force for $V = 600$ Vpp, $H = 0.1$ mm, and $f = 5000$ Hz.

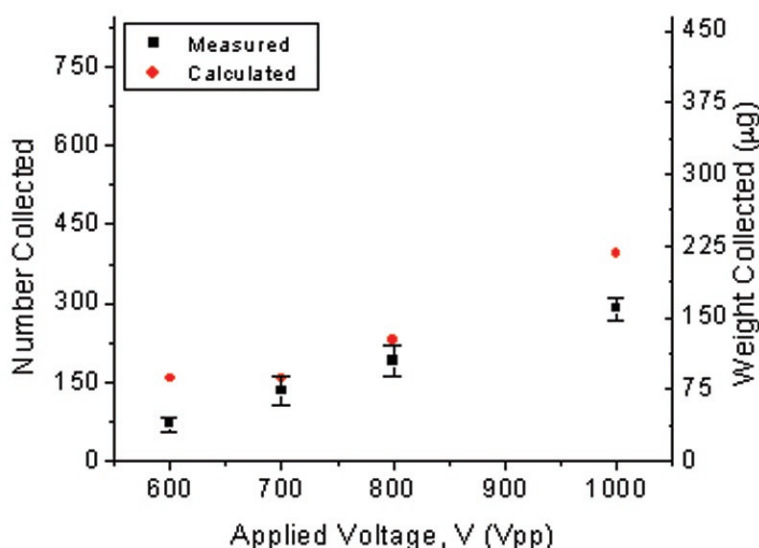


Figure 11: Total amount of powder collected as a function of the magnitude of the applied voltage, V , at a constant initial separation of 0.1 mm, and a frequency of 5000 Hz.

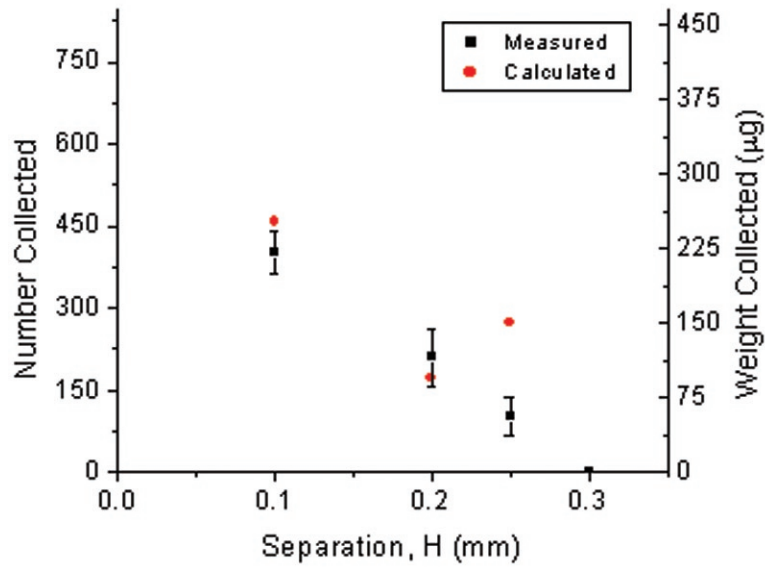


Figure 12: Total amount of powder collected as a function of the initial separation, H , at a constant applied voltage of 1100 Vpp, and a frequency of 5000 Hz.

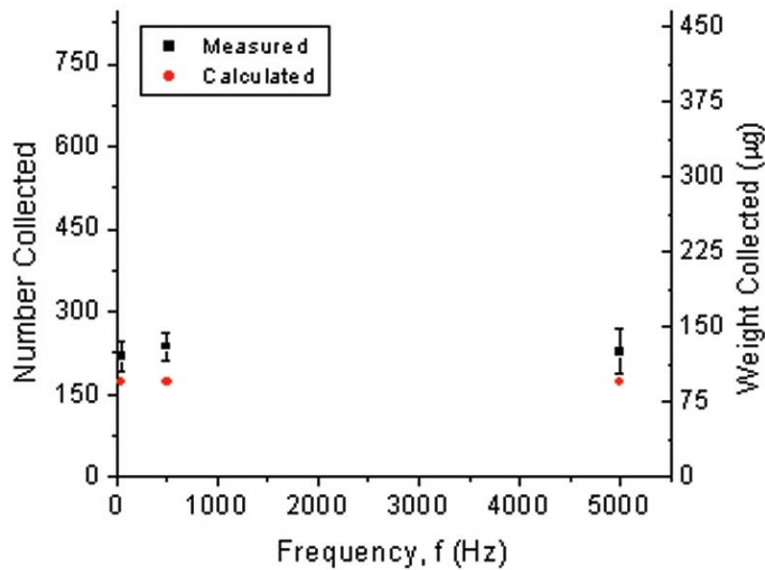


Figure 13: Total amount of powder collected as a function of the frequency, f , of the applied voltage at a constant applied voltage of 1100 Vpp, and an initial separation of 0.2 mm.

Results of the surface characterization experiments conducted for the fluidic assembly of micron scale silica particles are shown below in Figure 14. Streaming potential measurements conducted over different ionic strengths indicated an isoelectric point of the sapphire substrate at a pH of near 4.5. The data also reveal that the zeta potential is relatively invariant over the range of ionic strengths studied. The isoelectric point of the silica particles is slightly lower, as is shown in the results of microelectrophoresis experiments given in Figure 15. The zeta potential of silica is also substantially reduced with increasing ionic strength. This is expected from the collapse of the double layer with increasing salt concentration, pushing the potential at the shear plane closer to the surface potential under these conditions.

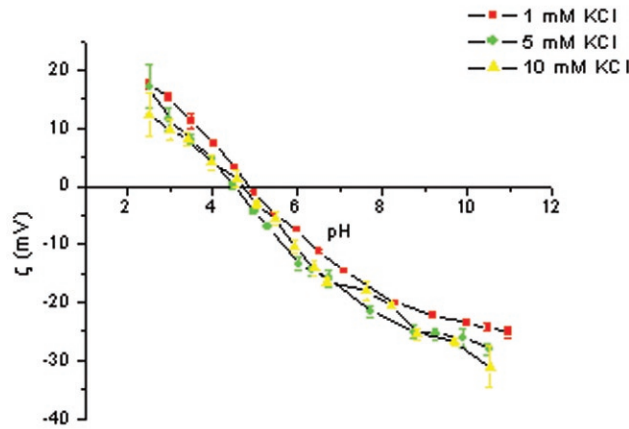


Figure 14: Zeta potential vs. pH as a function of ionic strength for the sapphire substrate.

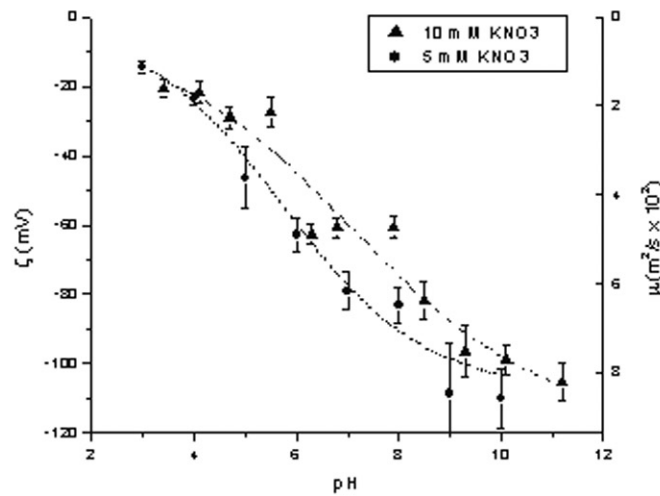


Figure 15: Zeta potential and corresponding mobility of 1.58 μm silica particles measured by microelectrophoresis.

A measurement of the conductivity of the solution over the range of pH and ionic strength studied was performed to verify that the background electrolyte concentration was indeed sufficient to maintain a constant conductivity. This is shown in Figure 16. The conductivity varies only with ionic strength and is independent of pH up to a value of 10, above which there is a significant contribution to the conductivity from the added base at higher pH values. This effect is more pronounced at the lower ionic strength, defining a lower limit for the salt concentration of interest in the electrophoretic deposition experiments.

The results of the adhesion of silica particles to the substrate over time are given in Figure 17 for two different ionic strengths. The fraction of mobile particles obtained from direct observation of adhesion using digital video microscopy is plotted at each time and pH. The onset of adhesion was experimentally observed to occur at a lower pH with increasing ionic strength. Nearly all of the particles were found in the adhered state below some critical pH. This value corresponds to the measured iso-electric point of the sapphire substrate, below which the particles and substrate carry surface charges that are opposite in sign. Above the iso-electric point of sapphire both the particles and substrate are negatively charged

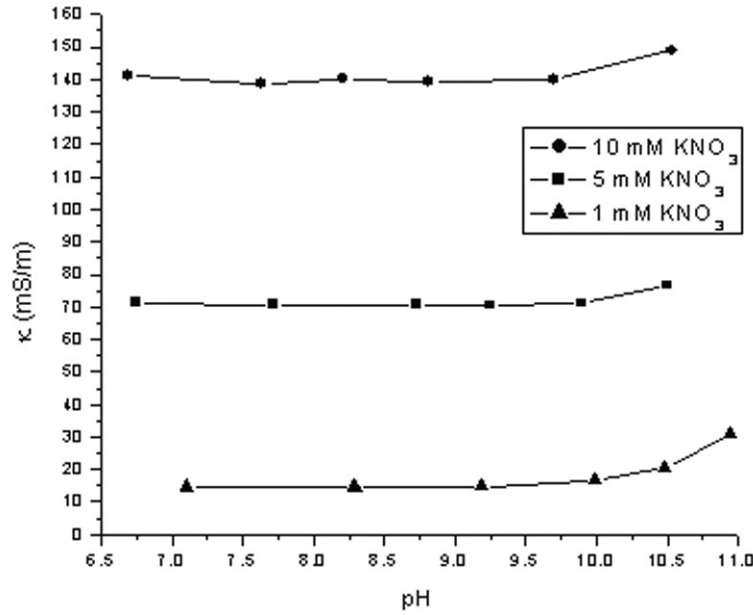
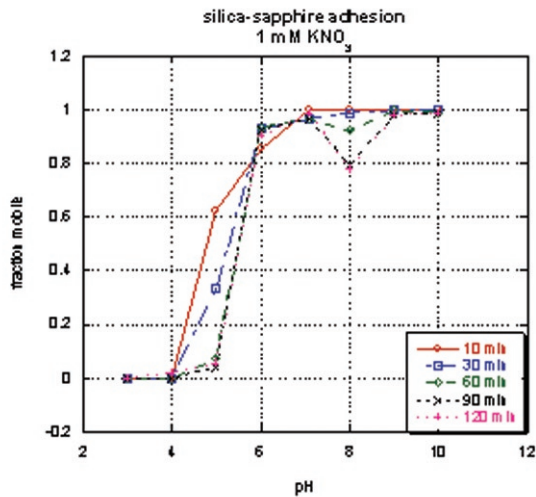
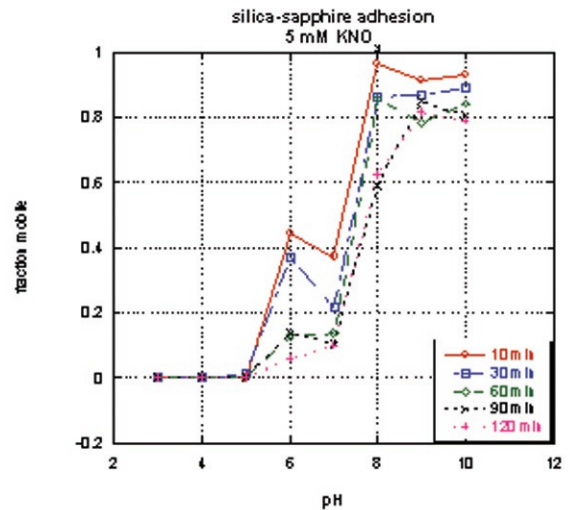


Figure 16: Variation of conductivity of particle suspension as a function of pH and ionic strength.

and the particles would be expected to remain mobile for a longer period of time. These experiments define the effective operating space over which substantial adhesion of particles may be avoided during electrophoretic deposition experiments. Further work is needed to fully understand the nature of the observed adhesion phenomenon near the anode during application of an electrical potential.



(a)



(b)

Figure 17: Variation of conductivity of particle suspension as a function of pH and ionic strength at (a) 1 mM KNO₃ and (b) 5 mM KNO₃.

Results of electrophoretic deposition experiments between the parallel electrode structures showed a dependence of particle mobility on the ionic strength of the background electrolyte, as shown in Figure 18. This is explained in terms of competing electro-hydrodynamic flows due to the electric field induced flow of counter-ions at the sapphire substrate which act to oppose the motion of the negatively charged particles. A schematic of this theory is shown in Figure 19. Further work is necessary to isolate the exact nature of

these competing flows and to investigate the sensitivity of the process to small variations in pH. A series of experiments using microelectrodes patterned on a quartz surface have been proposed in order to evaluate the effects of particles moving on a surface that is likely to exhibit similar surface chemistry.

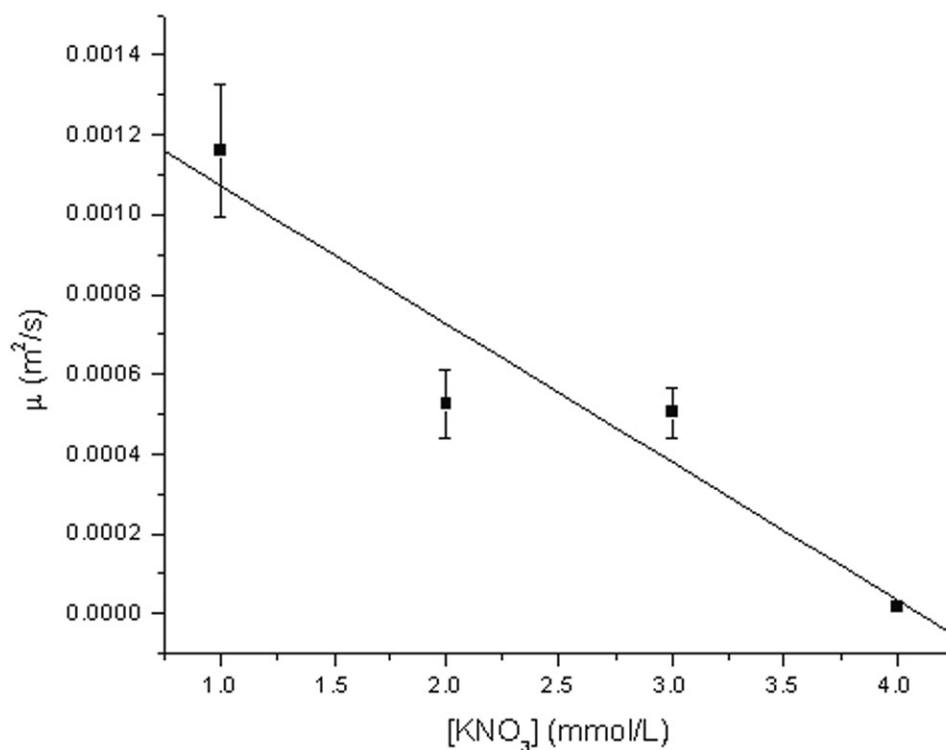


Figure 18: Variation in mobility of 1.58 μm silica particles due to applied DC field between microelectrodes as a function of ionic strength. The field was 3500 V/m.

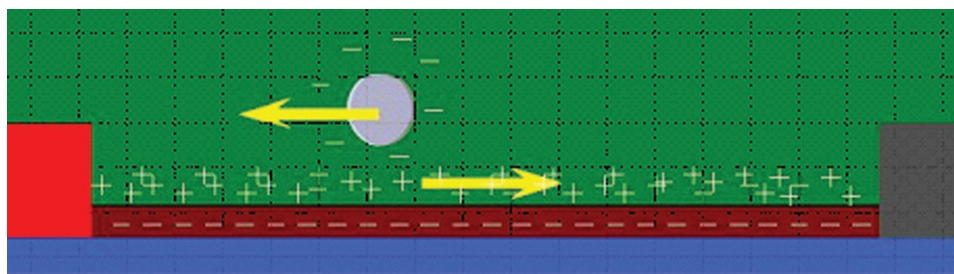


Figure 19: Schematic of competing electro-hydrodynamic flows due to accumulation of counter-ions just outside the electrical double layer of the sapphire substrate. The particles are attracted towards the anode, shown at left.

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DENDRITIC GROWTH WITH FLUID FLOW FOR PURE MATERIALS*

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Introduction

Dendritic growth is important because it is the basic microstructural pattern in solidified metals. The pattern selected during solidification of a pure material depends on the existing thermal field during freezing. Once this pattern is set, it is difficult to change in the solid state without substantial effort, e.g., through mechanical deformation and heat treatment.

The evolution of dendritic microstructures is reasonably well understood for pure materials growing into undercooled melts under purely diffusive conditions, i.e., when fluid flow is absent. The tip of the dendrite approximates a paraboloid of revolution. Ivantsov [1] determined the solution for the thermal field surrounding an isothermal dendrite, neglecting surface tension, and determined a relation between undercooling and the (constant) tip velocity and tip. The function is a combination of exponentials and error integrals, whose form is well known and not important for the current discussion. Since the tip radius and velocity appear only as a product, the diffusion solution does not uniquely determine the shape.

The pattern selection problem is resolved by including surface tension and its anisotropy in the boundary condition for the temperature of the dendrite, and relaxing the assumption that the shape is known. [2,3] This body of theory is known as “microscopic solvability.” In 2-D, it gives a correction to the shape of the interface near the tip, converging to the Ivantsov solution far away from the tip where curvature becomes negligible. The theory provides a second relation for the dendrite tip velocity and radius. The problem is somewhat more complicated in 3-D, where corrections to the Ivantsov shape are large. See Brener [4] for a treatment of this problem.

Recent numerical calculations using the phase field method, in two dimensions and at high undercooling, agree very well with the predictions of microscopic solvability theory. [5,6] At low undercooling, the computed selection constant still agrees with the theory, but the tip radius and tip velocity differ. Provatas et al [6] showed that this discrepancy arises because the transport solution at low undercooling does not satisfy the premise, assumed in solvability theory, that the dendrite is a single, isolated branch, independent of its neighbors. This may explain the difference between the predictions of microscopic solvability theory and experimental observations, which are invariably made at low undercooling.

The microstructure is significantly altered by the presence of flow during solidification. [7,8] This problem is important because flow induced by buoyancy, residual pouring currents or forced flow is nearly always

***Note: This is a condensation of an article that will appear shortly in *Metallurgical and Materials Transactions*. All figures and equations have been deleted for this presentation.**

Keywords: dendrites, 3-D, phase-field, parallel computing

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present in castings unless great pains are taken to avoid it, for example by performing experiments in the reduced gravity of outer space. Saville and Beaghton [9] extended the theory of Ivantsov to consider the case of an isolated paraboloid of revolution, with zero surface tension, growing in a shape preserving way at constant velocity, with a uniform forced flow from infinity aligned parallel to the growth axis. The characteristic parameters for this problem are such that the flow is dominated by viscous forces, but the transport is dominated by advection. The flow is therefore well approximated by Oseen's equation, and Saville and Beaghton presented a solution where the tip velocity and radius are still not uniquely determined by the transport solution, and a selection criterion is still required.

Bouissou and Pelcé [10] examined the stability of a 2-D dendrite under the assumptions of Saville and Beaghton's analysis, and determined the scaling of the selection constant with flow. The applicability of this theory is not yet confirmed by either computations or experiments. A recent study by Beckermann et al [11] found a weak dependence of the selection constant on flow, but neither confirmed nor negated the theory. The existing experimental evidence is also inconclusive, and perhaps contradictory. Bouissou et al [12] examined the flow of a dilute pivalic acid-ethanol (PVA-EtOH) solution past a solidifying PVA dendrite, and found a trend similar to that predicted by their theory. On the other hand, in a series of experiments using pure succinonitrile (SCN), Lee et al [13] found that the selection constant increased with flow velocity. These discrepancies are currently unexplained, and in this paper we perform simulations intended to shed some light on this issue. We use the phase field method, which we now describe briefly before proceeding to a more detailed description of our simulations.

The phase field method has become the method of choice for simulating dendritic growth, because of its ability to handle the complex evolving shape of the dendrite. [14,15,16,17,18] Because this method has been described in detail in numerous articles, we present here just a brief sketch. The dendrite growth problem follows the evolution of the solid from the liquid. In the so-called sharp interface problem, the liquid-solid interface must satisfy two boundary conditions: thermodynamic equilibrium, which requires that the interface temperature satisfy the Gibbs-Thomson condition including crystalline anisotropy

Solution of the sharp interface problem for dendritic growth is difficult, because it requires that the moving boundary be tracked explicitly. In the phase field method, a continuous order parameter is introduced, such that -1 corresponds to the liquid, +1 corresponds to the solid, and the set of locations where the parameter is 0 corresponds to the interface between the two phases. The liquid-solid interface is diffuse, with nominal thickness W_0 . For a more detailed discussion of the method, the specific models used, and a description of convergence of the phase field model to the sharp interface, see Karma and Rappel [5], Beckermann et al [11] and Jeong et al [19].

The phase field method introduces an artificial finite width for the interface. Karma and Rappel [5] demonstrated convergence of the phase field model to the sharp interface model in the limit where the interface width is much less than the diffusion length, and gave specific formulas for relating the parameters in the two problems. Grid convergence of the numerical solution requires that the grid spacing be much less than the interface width *and* also that the domain size be much larger than the diffusion length. See Karma and Rappel [5] for further details. The important result is that these two requirements force us to choose the domain to be 1000 or more times the grid spacing. Thus, a uniform mesh would require on the order of 10^6 grid points in 2D, and 10^9 in 3D.

We finesse the length scale problem by solving the equations on an adaptive grid, providing high resolution near the interface, and a coarser mesh further away to resolve the diffusion field. The methods have been described elsewhere [6,19], and so we provide only a limited discussion in this article, in the next section. Plapp and Karma [20] developed a different approach, where they solve the phase field model on a regular inner grid, and resolve the outer diffusion field using a Monte-Carlo method, with the two solutions matched at an artificial boundary. Both methods are effective for the diffusion problem, but the extension of the latter method to cases where fluid flow is present is not obvious. Accordingly, we focus the rest of our discussion on the solution of the solidification problem with melt convection using our adaptive grid techniques.

It is important to understand that in order to compare our numerical calculations with experiments, we must perform simulations in three dimensions, at low undercooling, and for materials of low anisotropy. Each one of these choices makes the problem computationally more difficult, and the combination represents a formidable challenge. We have developed a code which solves the 3D Navier-Stokes, energy and phase field equations on an adaptive grid in parallel. [19] This is essential for us to take up the problems we have described.

In the next section, we give an abbreviated description of the phase-field model, and its numerical implementation. We then describe the results of simulations relevant to the experiments of Lee et al [13] and Bouissou et al [12].

Methods

The phase field method has been extended to include fluid flow in the melt along with solidification. [21,22,11,19] The essential new features, in addition to solving the Navier-Stokes equations in the fluid phase, are the formulation of the model such that the velocity is extinguished in the solid phase, and ensuring that the interfacial shear stress is correctly represented. Tönhardt et al [21] and Juric [22] use an enhanced viscosity approach to extinguish the velocity in the solid phase. In this approach, the viscosity changes rapidly from its value in the melt to a very large value representing the solid, as the phase field goes from -1 to 1. This method is effective, but convergence can be very sensitive to the relative magnitude of the viscosity change and the interface thickness.

We adopt the method of Beckermann et al [11], who introduced a mixture formulation for the continuity, Navier-Stokes and energy equations. An interfacial stress term is added to the Navier-Stokes to ensure that the shear stress is correct at the interface. See Beckermann et al [11] for further details.

The important physical parameters in the simulations are the thermal diffusivity, capillary length and surface tension anisotropy. The phase field model introduces the additional non-physical parameters of the grid spacing, interface width and domain size. Karma and Rappel [5] presented an asymptotic analysis to show the relations between the parameters such that the phase field model converges to the sharp interface model.

We solve the 3D flow equations using the Semi-Implicit Approximate Projection Method (SIAPM)[23], a predictor-corrector method which can solve these equations effectively, especially for large 3D problems, using relatively small amounts of memory. For a detailed discussion of the algorithm, the reader is referred to the original paper [23], and for a detailed description of the parallel adaptive finite element implementation, see Jeong et al [19].

The equations are solved in a segregated fashion, using an implicit time-stepping scheme, except for the phase-field equation, which we solve explicitly. The grid is adapted so that it is finest in the vicinity of the interface, where the grid spacing must resolve the interface width W_0 , to a much coarser mesh far away, where all of the primitive fields vary slowly. The typical ratio of largest to smallest element size in our calculations is 512, but there is no inherent limit. Element refinement and fusion is done based on the value of an error estimator, computed from the solution within each element. The details of the procedure are given in Jeong et al [19], and are not repeated here. The grid was adapted whenever the dendrite tip moved a predetermined distance, typically $0.4W_0$.

The basic problem which we solve places a small spherical seed at the centroid of a cube, with the axes of crystalline symmetry aligned with the cube edges. Earlier work has demonstrated that when the grid spacings are chosen as described earlier, grid anisotropy is minimal, and the seed orientation is merely a matter of convenience. Flow is introduced on the front face of the cube as a uniform velocity. The lateral faces are all assumed to be planes of symmetry, and the exit face has zero shear stress. The temperature on all faces of the computational domain is set to the undercooling, and we always use a domain of edge length sufficiently large that the thermal and velocity boundary conditions do not affect the result.

A convenient measure of the results is to track the evolution of the tip velocity and tip radius in the various directions. Simulations in both 2D [11] and 3D [19] showed that the tip velocity is increased on the leading arm, decreased on the trailing arm, and essentially unchanged on the transverse arms. We introduced a few “tricks” to speed up the calculations, and these are described now, using the leading and trailing tip velocities as indicators of the validity of these techniques.

We use a different time step size to solve the various equations. The phase-field and temperature equations are solved using the minimum time step and the fluid flow equations are solved using a larger time step. The physical basis for this choice is that the interface moves very slowly relative to the fluid, and thus the motion of the interface does not strongly affect the flow field. The results were indistinguishable for ratios up to about 10 for relatively high speed growth, and up to a ratio of 25 for very low speed growth such as in SCN at low undercooling. This provides a substantial computational savings compared to using a single time step for all of the fields. In order to further reduce computation time, we also use a technique where we start the computations with flow using a seed that had been grown to small, but finite size without flow. The tip velocity for a dendrite started from the precursor seed quickly recovers to the solution where flow was present from the beginning, and the results are indistinguishable. The dendrite tip radius shows the same trend.

Results

The simulations we report in this section were run to examine the role of fluid flow on dendrite growth at low undercooling, for comparison with experiments. We present results for the cases shown in Table 1. The value of anisotropy equal to 0.0055 corresponds to SCN, while anisotropy equal to 0.025 corresponds to PVA. We note that these values have not been corrected for grid anisotropy. The results presented below should nevertheless be viewed as approximate in this sense.

Table 1: Parameters for simulations reported in this section

Case	Anisotropy	Undercooling	U (cm/s)
1a	0.0055	0.04	0
b			0.5
c			1.0
2a	0.025	0.05	0
b			0.12
c			0.24
d			0.60

The simulations were run on a variety of machines: Sun Ultra-2/200 MHz, IBM RS/6000 7043 Model 260, and SGI Origin 2000 multiprocessor machines. Comparisons of cpu time for the various cases are therefore not meaningful. The parallel runs on the SGI Origin 2000 were usually made as a series of restart/batch jobs in order to optimize throughput in the queing system. Statistics for one run (Case 1c), which should be considered representative, are that the run took 2,496 cpu hours on 32 processors, 101 clock hours (average parallel efficiency of 77%), and used about 2 Gb of memory distributed over the 32 processors.

Succinonitrile

With flow, the tip velocity increases dramatically, and tip radius decreases dramatically, immediately as the flow is started. The simulations do not appear to have reached a final steady state, but the temporal variation is small at the end of the simulations. (The simulations were terminated when the mesh size grew to about 450,000 nodes). The selection constant reaches its final value much more quickly than either the tip velocity or radius, which is also characteristic of calculations in the absence of flow. We find that the selection constant decreases slightly with flow.

Table 2 compares the computed values with those obtained experimentally by Lee et al. [13] The results are presented as ratios of the final value in the simulations to the corresponding value without flow. Note that our simulations are not fully converged. Whereas the ratios of tip velocities and tip radii are quite similar in both the simulations and the experiments, the trends in the selection constant are opposite, i.e. we find it to be a weakly decreasing function of the far-field velocity, while Lee, et al. found it to be an increasing function of flow velocity.

Table 2: Comparison of computed and experimental tip parameters for succinonitrile.

	Flow velocity (cm/s)	Tip velocity ratio	Tip radius ratio	Selection constant ratio
Expt	1.0	2.2	0.6	1.4
Calc		2.6	0.72	0.8
Expt	0.5	1.7	0.71	1.2
Calc		2.1	0.71	0.95

Finally, it is instructive to compare the results of the calculations with the solution of Beaghton and Saville. Although there is no unique state determined by their theory, the computed solution might be expected to follow their transport solution. When the tip radius is computed using the exact computed shape of the dendrite, the results are quite far from the Oseen-Ivantsov solution. Beckermann et al. [11] showed that the tip radii should be corrected to compute a smooth paraboloidal shape near the tip for comparison to the transport solution. For this case, however, because the tip is so broad, the shape correction has almost no effect.

While the trends are similar, none of the curves matches very well. This is important, because it shows that neither the experiments nor the calculations match the transport solution for an isolated paraboloid of revolution. We believe that the explanation for this is that neither the computed nor experimental dendrites are well approximated as paraboloids, and therefore the temperature field should not be expected to match the transport solution. It is also possible that the transverse arms affect the flow, an effect not accounted for at all in the Oseen-Ivantsov theory. We observed this phenomenon in diffusive growth at low undercooling [24].

PVA

We also considered several cases at higher anisotropy of 0.025, corresponding to PVA. At high undercooling (0.55), our results are similar to those reported by Beckermann et al, whose simulations were done in 2D, but were otherwise similar to our 3D analyses. The results compare reasonably well to the Oseen-Ivantsov. In this case, where the dendrite tip is much sharper than it was for SCN, the parabolic tip curvature correction brings the results into agreement with the Oseen-Ivantsov transport solution. This occurs because at high values of anisotropy and undercooling the computed shape tends to look much more like the isolated paraboloid in the analytical solution, than it does for smaller values of the parameters.

We note that we cannot compare these calculations directly with the experiments of Bouissou et al, for several reasons. Their experiments were performed in an alloy system, and at present we compute only for pure materials. Further, their experiments were performed by growing dendrites in a narrow gap, much thinner than the boundary layers in that direction for a freely growing dendrite. We will examine this case in a later paper.

For PVA at low undercooling, similar trends are observed for PVA as in SCN, i.e. the dendrite tip velocity increases and tip radius decreases as flow velocity increases. Once again, the selection constant is a weakly decreasing function of flow velocity, which reaches a steady value much sooner than either tip radius or velocity. The isotherms are once again advected by the flow, but the tip shape is much smoother for PVA than for SCN. There are still systematic deviations from the Oseen-Ivanstov solution.

Discussion

The most important observation from our computations is that significant discrepancies exist between the analytical theory of Saville and Beaghton for an isolated branchless dendrite, our calculations *and* the available experimental results. We believe that the source of these differences lies in the difference between the real shape of a growing dendrite, and the assumed branchless, isolated paraboloid.

Much has been made about the trend in the selection constant with increasing imposed flow. We find a very weak negative dependence of on flow velocity, i.e., the selection constant decreases slightly as flow

velocity increases. We note that even though the selection constant is nearly constant, the tip velocity increases substantially, and the tip radius decreases significantly. Within the precision of our calculations, the selection constant is essentially constant. This result is consistent with the theory of Bouissou and Pelcé.

There were significant deviations between the theory of Saville and Beaghton and *both* our calculations and the experiments of Lee et al [13]. We believe that the difference arises from the idealization of the dendrite as an isolated paraboloidal shape. For low Reynolds numbers, we expect to find a viscous boundary layer ahead of any obstacle, including sidebranches and transverse arms. For the example cited in the preceding paragraph, the boundary layer is larger than the distance to the transverse arms in our computations, and probably also in the experiments. Thus, if the flow field is significantly different from the Oseen-Ivantsov solution, one cannot expect the results to match the theory. The flow reacts to the entire body of the dendrite, not just the tip. We note that this effect would be even more pronounced in two dimensions, where flow around the dendrite tip cannot occur.

Our conclusion from this is that both the experiments and the calculations are very difficult to perform in such a way as to satisfy the idealized conditions assumed in the theory, and this clouds our ability to make precise statements about the theory of tip selection under conditions of forced flow.

Conclusion

We have developed a three-dimensional, adaptive, parallel finite element code to examine solidification of pure materials under conditions of forced flow. We have examined the effect of undercooling, surface tension anisotropy and imposed flow velocity on the growth. The flow significantly alters the growth process, producing dendrites that grow faster, and with greater tip curvature, into the flow. The selection constant decreases slightly with flow velocity in our calculations.

The results of the calculations agree well with the transport solution of Saville and Beaghton [9] at high undercooling and high anisotropy. At low undercooling, significant deviations are found. We attribute this difference to the influence of other parts of the dendrite, removed from the tip, on the flow field.

Acknowledgment

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KINETICS OF NUCLEATION AND CRYSTAL GROWTH IN GLASS FORMING MELTS IN MICROGRAVITY

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Introduction

This flight definition project has the specific objective of investigating the kinetics of nucleation and crystal growth in high temperature inorganic oxide, glass forming melts in microgravity. It is related to one¹ of our previous NASA projects that was concerned with glass formation for high temperature containerless melts in microgravity. The previous work culminated in two experiments^{2,3} which were conducted aboard the space shuttle in 1983 and 1985 and which consisted of melting (at 1500° C) and cooling levitated 6 to 8 mm diameter spherical samples in a Single Axis Acoustic Levitator (SAAL) furnace.

Compared to other types of materials, there have been relatively few experiments, 6 to 8, conducted on inorganic glasses in space. These experiments²⁻¹¹ have been concerned with mass transport (alkali diffusion), containerless melting, critical cooling rate for glass formation, chemical homogeneity, fiber pulling, and crystallization of glass forming melts. One of the most important and consistent findings in all of these experiments has been that the glasses prepared in microgravity are more resistant to crystallization (better glass former) and more chemically homogeneous than equivalent glasses made on earth (1g). The chemical composition of the melt appears relatively unimportant since the same general results have been reported for oxide, fluoride and chalcogenide melts. These results for space-processed glasses have important implications, since glasses with a higher resistance to crystallization or higher chemical homogeneity than those attainable on earth can significantly advance applications in areas such as fiber optics communications, high power laser glasses, and other photonic devices where glasses are the key functional materials.

The classical theories for nucleation and crystal growth for a glass or melt do not contain any parameter that is directly dependent upon the g-value, so it is not readily apparent why glasses prepared in microgravity should be more resistant to crystallization than equivalent glasses prepared on earth. Similarly, the gravity-driven convection in a fluid melt is believed to be the primary force field that is responsible for melt homogenization on earth. Thus, it is not obvious why a glass prepared in space, where gravity-driven convection is ideally absent, would be more chemically homogeneous than a glass identically prepared on earth. The primary *objective* of the present research is,

To obtain experimental data for the nucleation rate and crystal growth rate for a well characterized silicate melt (lithium disilicate) processed entirely in space (low gravity) and compare these rates with the nucleation and crystal growth rates for a similar glass prepared identically on earth (1g).

Keywords: glass, nucleation and crystal growth rates, shear thinning, low gravity

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The nucleation and crystal growth rates for a melt prepared in space have never been measured directly, but such data are expected to explain (at least partially) these puzzling, but extremely interesting results that have great scientific and practical relevance to the development, manufacturing, and use of inorganic glasses, glass-ceramics, the new bulk metallic glasses (BMG), and other solids derived from a melt.

Hypothesis

The reason why space glasses appear to be more resistant to crystallization than identical glasses prepared on earth is not known at this time, but “shear thinning” is suspected to be a likely reason. “Shear thinning” is the reduction in viscosity, which occurs with increasing shear rate in non-Newtonian liquids at a constant temperature as shown in Fig. 1. Such a reduction in viscosity with increasing shear rate has been reported for several commercial glasses¹²⁻¹⁴, including the lithium disilicate (LS₂) composition^{15, 16} that will be used in our space experiments. The reported¹⁶ decrease in viscosity with increasing shear rate for a LS₂ glass is shown in Fig. 1. We believe that the gravity-driven convection that is normally present to some degree in a melt on earth will be much smaller or ideally absent in a nearly stagnant (quiescent) melt in space. A more quiescent melt in space should experience a smaller (or negligible) shear rate and, consequently, have a higher viscosity (less shear thinning) than a melt on earth at the same temperature as schematically shown in Fig. 2. A higher viscosity for the space glass would be expected to make it more resistant to crystallization because of the smaller nucleation and crystal growth rates, see Fig. 2.

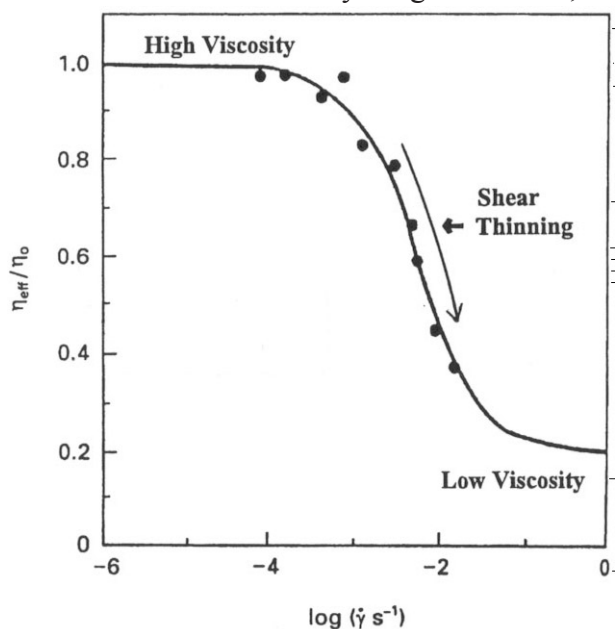


Fig. 1. Change in the effective viscosity (η_{eff}) with shear rate $\dot{\gamma}$ for a Li₂O.2SiO₂ glass at 483° C ($\eta \sim 2.24 \times 10^{10}$ Pa.s). From ref. 18

Ground-Based Work on Shear Thinning

A. Modeling

Computer modeling for the rates of fluid flow and shear across a LS₂ melt contained in a platinum capsule of the same shape and size (cylindrical, 2.5 cm long and 1.0 cm in diameter) as those proposed for the flight experiments were performed in collaboration with Drs. N. Ramachandran of USRA and E. Ethridge of MSFC, NASA. The calculations were carried out using a FIDAP fluid dynamics package (Fluent Inc., version 8.0, 1998) assuming the platinum cylinder containing the melt was heated in such a way that a

thermal gradient existed at its two ends. The curved wall of the cylinder was assumed to be insulating and the gravity acting in a transverse direction to the thermal gradient. The results show that the shear rate decreases linearly with decreasing gravity for a constant temperature gradient across the melt and increases with increasing temperature gradient, see Fig. 3. This means that the shear rate for a glass prepared in space ($< 10^{-4} g$) will be at least four orders of magnitude less than that in the same glass prepared at 1g. Data for glasses such as LS_2 indicate that a reduction of four orders of magnitude in the shear rate for the space glass could cause the viscosity to increase from 2 to 10 times. Such an increase in viscosity could decrease the crystallization tendency (or increase the glass forming tendency) by factors from 16 to 10,000 compared to an identical glass prepared on earth.

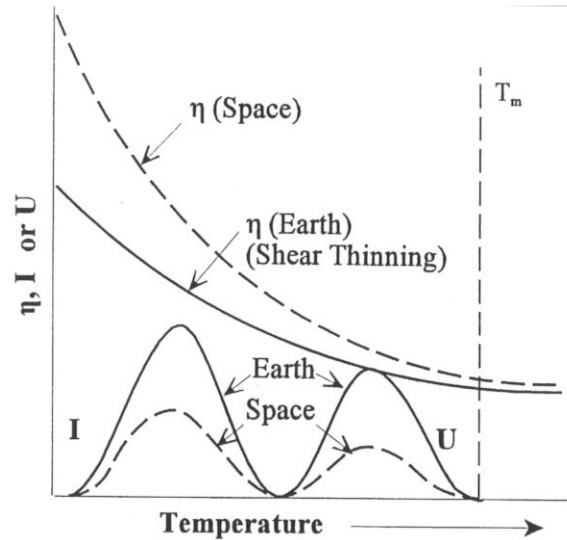


Fig. 2. Schematic representation of the anticipated viscosity (η), nucleation rate (I), and crystal growth rate (U) for a melt in space and for the identical melt on earth based on "shear thinning".

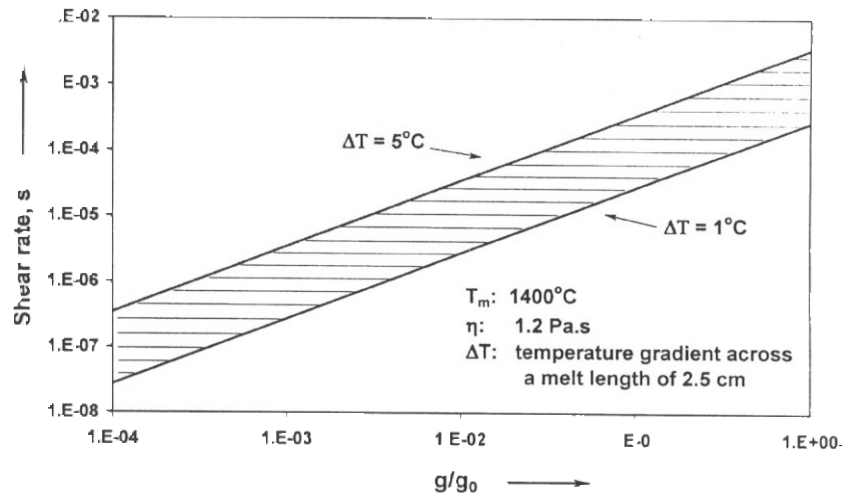


Fig. 3. Calculated shear rate for a $Li_2O.2SiO_2$ melt as a function of gravity.

B. Experiment

Experiments to verify the shear thinning hypothesis were performed by (isothermally) heating bent LS_2 glass fibers at temperatures (350 to $400^\circ C$) well below the temperatures for nucleation (425 to $500^\circ C$) and crystal growth ($> 570^\circ C$) for this glass. The glass fibers, $\sim 150 \mu m$ diameter and 12 cm long, were

bent and held between two fixed holes, ~ 2.5 cm apart, on a refractory block as shown schematically in Fig. 4. The flexural stress at the tip of the bent fibers will be the highest, estimated about 0.5 GPa in the present case. Straight glass fibers of the same $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ composition, which were not subjected to any kind of stress, were also heated simultaneously for comparison. The refractory block holding the glass fibers was inserted in a furnace already equilibrated at a preset temperature and held there for various times between 10 min and 4 h.

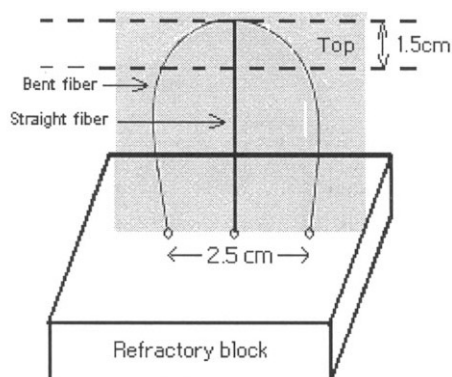


Fig. 4. Schematic of heat-treatment experiments of bent and straight $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass fibers.

When released after the heat treatment, the bent fibers were found to deform permanently as shown in Fig. 5 for the fibers heated at 370°C , and the deformation increased with increasing time for heat treatment. This 370°C temperature is much lower than the glass transition temperature ($\sim 460^\circ\text{C}$) for this glass, where viscosity is expected to be larger than 10^{14} Pa.s. The permanent deformation of the glass fibers indicates that a fluid flow might have been occurred, at least at the tip of the bent fibers, even at 370°C . This means that with the application of a bending stress, the viscosity of the glass decreased from its value of stress-free condition, which is a manifestation of shear thinning.

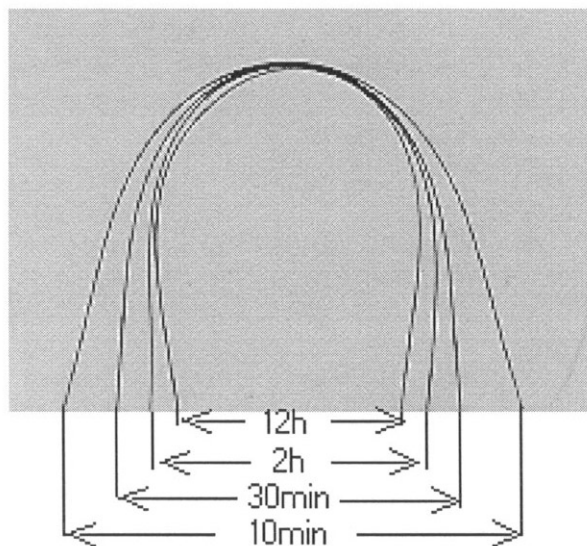


Fig. 5. Permanently deformed $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass fibers after heat-treatment at 370°C for the times shown.

Results from differential thermal analysis (DTA) also showed, Fig. 6, that the crystallization peak for the sample prepared from the tip of the bent fibers that were heated at 370°C for 3 h, was larger and occurred

at a lower temperature than those for the sample prepared from the identically heat treated straight fibers. Clearly, the tip of the bent fibers, where the bending stress was the highest, contained a higher number of nuclei than the stress-free, straight fibers. It is to be noted that the 370° C heat treatment temperature is about 55° C lower than the onset temperature (~ 425° C) for nucleation for this LS_2 glass, and no nuclei is expected to form when the glass is heated at 370° C. However, the DTA results in Fig. 6 indicate the formation of additional nuclei at the tip of the bent glass fibers, presumably due to a lowering of viscosity caused by the applied bending stress in this region of the fibers.

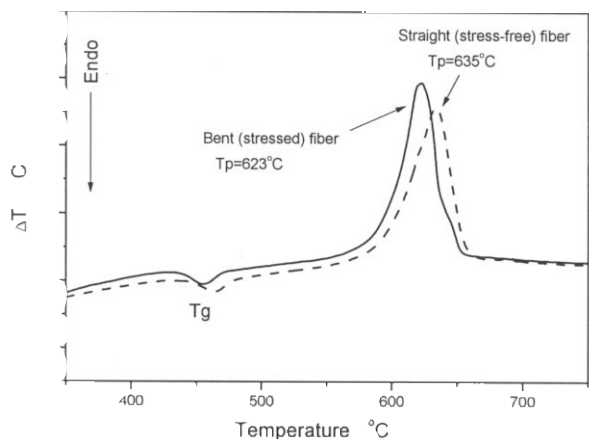


Fig. 6. Differential thermal analysis of the bent (stressed) and straight (stress-free) $Li_2O \cdot 2SiO_2$ glass fibers after heat-treatment at 370° C for 3 h.

Similar heat treatment experiments conducted for bent and straight LS_2 glass fibers at 450° C for 8 h, show visible crystallization at the tip of the fibers, see Fig. 7. This 450° C temperature is about 120° C lower than the onset temperature for crystallization for this glass, and, as expected, no such crystallization was observed on the stress-free, straight fibers, Fig. 8, which received a simultaneous and identical heat treatment as the bent fibers.

The above experiments clearly demonstrate that the tendency for nucleation and crystal growth in a LS_2 glass is increased when it is subjected to an external stress, and shear thinning, i.e., a decrease in viscosity with increasing stress, is suspected to be a reason for this. Further investigations for a quantitative determination of the nucleation and crystal growth rates as a function of stress at a constant temperature, as function of temperature at a constant stress, and the mechanism of stress relaxation for these LS_2 glass fibers are continuing.

Plans for Flight Experiments

The overall plan for the flight experiments will be to measure, for the first time, the nucleation rate (I) and the crystal growth rate (U), each at three different temperatures, for a $Li_2O \cdot 2SiO_2$ (LS_2) glass prepared completely in space, see Tables 1 and 2. The glasses prepared in space will be made by remelting a glass prepared on earth. A glass cylinder contained in a doubly sealed platinum cylinder (2.5 cm long and 1.0 cm in diameter) will be melted at 1400° C for 3 h and quenched to glass at an appropriate cooling rate. After melting and cooling, the encapsulated glass samples will be given a nucleation heat treatment at either 440, 455, or 470° C for 1 to 5 h and a crystal growth heat treatment at 590, 610, or 630° C for 10 to 30 min. The samples heat treated in space will be analyzed on earth to determine I and U which will be compared with the I and U values for glasses melted and heat treated (for nucleation and crystal growth) identically on earth.

The traditional method^{17, 18}, which requires measuring the number or size of crystals by optical microscopy on polished sections of the heat treated samples, will generally be used to determine I and U. A newly developed alternative method^{19, 20} which uses differential thermal analysis (DTA) and which has several advantages (faster, smaller amount of samples, less complexity for sample processing) over the traditional method will also be used for measuring I and U.

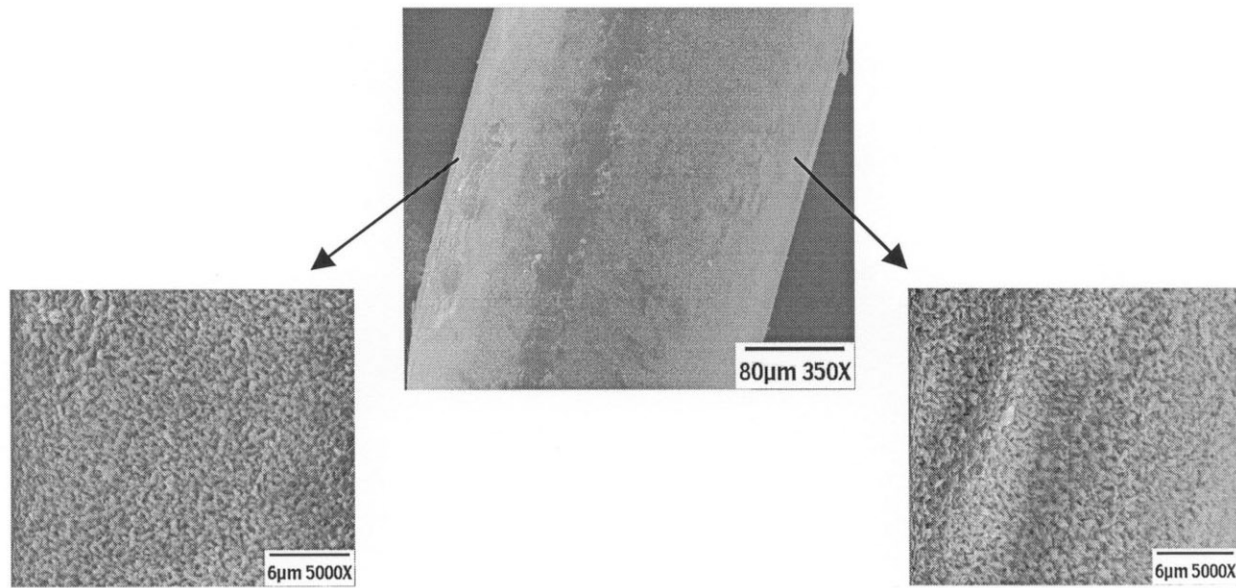


Fig. 7. Crystallization in $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ bent (stressed) glass fibers when heat-treated at 450°C for 8 h.

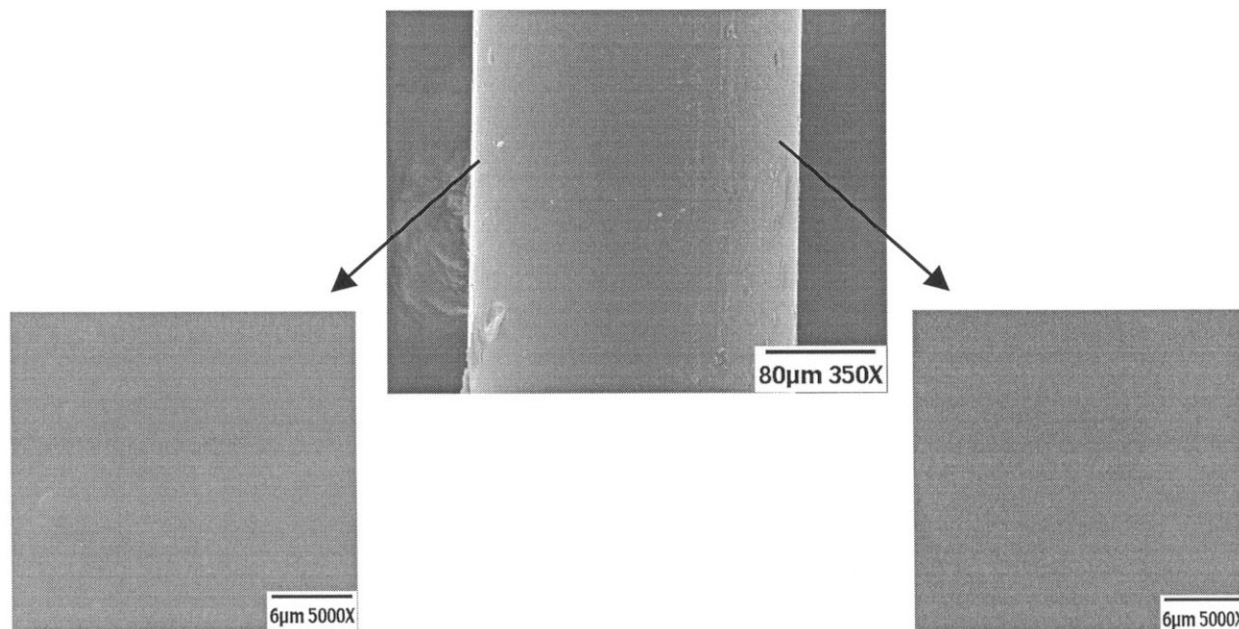


Fig. 8. A $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ straight (stress-free) glass fiber after heat treatment at 450°C for 8 h (the same heat-treatment as received by the bent fiber in Fig. 7). The 450°C is about 120°C lower than the onset temperature for crystallization of this glass, and, as expected, no visible crystallization was observed in this stress-free fiber.

Some of the glass samples melted in space in platinum capsules will be returned to earth in their as-quenched condition (i.e., without any heat treatment for nucleation and crystal growth in space) for 152

structural evaluation, measuring specific properties, and determining the concentration of quenched-in nuclei (N_q) in these glasses (samples in the bottom row of Tables 1 and 2). A comparison of N_q in the space and earth melted glasses will provide qualitative information on the degree of chemical homogeneity in these glasses. A glass containing a colored (blue) spot on its surface (sample B in Tables 1 and 2) will also be remelted in space for assessing the extent of fluid flow in high temperature melts in microgravity. Any movement of the blue spot in the melt will leave a blue trail in the melt.

Table 1. Experimental plans for measuring nucleation rate (I) for a LS_2 glass in space (samples are doubly sealed in platinum capsules).

Sample Type	Melting in Space Temp./Time	Nucleation				Crystal Development Temp./Time
		Temp. °C	Time, Hour			
			1	3	5	
A	1400 °C/3h	440	√	√	√	600 °C/20 min
		455	√	√	√	
		470	√	√	√	
A	None (Melted on earth)	440	√	√	√	
		455	√	√	√	
		470	√	√	√	
A,B	1400 °C/3h	None (A-N, B-N)				None

Table 2. Experimental plans for measuring crystal growth rate (U) for a LS_2 glass in space (samples are doubly sealed in platinum capsules).

Sample Type	Melting in Space Temp./Time	Nucleation Temp./Time	Crystal Growth			
			Temp. °C	Time, Min.		
				10	20	30
A	1400 °C/3h	455 °C/30 min	590	√	√	√
			610	√	√	√
			630	√	√	√
A	None (Melted on earth)	455 °C/30 min	590	√	√	√
			610	√	√	√
			630	√	√	√
A,B	1400 °C/3h	None	None (A-N, B-N)			

A, Glass premelted on earth.

B, Glass premelted on earth with a colored spot.

A-N, B-N: Melted in space, but no nucleation or crystal growth heat treatment in space.

Comments

If the values for I and U for the LS_2 glass prepared in microgravity are indeed found to be smaller than the glass made on earth, then our understanding of the fundamental processes for nucleation and crystal growth in glasses will be greatly improved. The classical equations for I and U may need to be modified to account for differences in gravity through the viscosity term in these equations. This enhanced understanding of the

fundamental mechanisms for glass formation, nucleation, and crystallization could lead to improvements in present-day glass processing technology on earth, thereby, improving our ability to produce glasses of higher quality and improved properties.

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RECOVERY OF MINERALS IN MARTIAN SOILS VIA SUPERCRITICAL FLUID EXTRACTION

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This investigation involves the determination of the solubilities of inorganic compounds in supercritical carbon dioxide, which is basic property information of these inorganic compounds. If there are inorganic compounds which have associated with them water of hydration which are soluble in supercritical carbon dioxide, then a process which extracts these compounds in supercritical carbon dioxide could be developed to recover water on Mars. In addition, supercritical carbon dioxide may react with certain inorganic compounds producing water as a by-product of the reaction

Technical Objectives

The objective of this work is the development of a supercritical CO₂ process for the recovery of minerals from Martian soils. Samples of the simulant JSC Mars-1 were obtained from the Johnson Space Center. Additional compounds such as metal chlorides, sulfates, and hydrated sulfates, nitrates, carbonates, and oxides have been tested for solubility based on the current knowledge of Martian soils. The solubility of minerals and compounds in supercritical CO₂ was determined as a function of temperature and pressure. The solubility data will be modeled using the Peng-Robinson or Redlich-Kwong equations; solvent interaction parameters will be regressed from experimental data.

Experimental Procedures and Results

We obtained samples of JSC Mars-1. This simulated Martian regolith was extracted using supercritical CO₂. In our experimental procedure to screen samples for solubility in supercritical carbon dioxide, we take about 1 gram of sample, place it in the sample cell of our ISCO extractor, shown in Figure. 1.

Supercritical carbon dioxide is pumped through the extraction cell at a flowrate of about 1ml/min. The pressure and temperature are controlled. The temperature and pressure range are 35-145 C and 50-240 Bar. As shown in Figure. 2, approximately 5.5% was extracted at 35°C. At 120°C, 13% was extracted, as compared to 8% by heating in a furnace. Analysis of this complex material has not yet been performed. Figures. 3 and 4 are Thermal Gravimetric Analysis (TGA) results and Differential Scanning Calorimetry (DSC) results for the JSC Mars-1 simulant. The change, either from reaction, vaporization, latent heats of structure rearrangement, or combinations are indicated by the 177.3J/g energy determined by the DSC.

We began to screen inorganic compounds such as metal sulfates, chlorides, nitrates, etc. In our experimental procedure to screen samples for solubility in supercritical carbon dioxide, we take about 1 gram of sample, place it in the sample cell of our ISCO extractor, shown in Figure. 1. Supercritical carbon dioxide is pumped through the extraction cell at a flowrate of about 1ml/min. The pressure and temperature are controlled. The temperature and pressure range are 35-145 C and 50-240 Bar. The carbon dioxide exiting

Keywords: water on mars, extracting minerals on mars, supercritical extraction, ISRU

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the extractor is bubbled through water contained in a glass tube. The aqueous solution in the tube can then be analyzed via ICP for metals. TGA and DSC are also run on these samples to compare the results of heating in a nitrogen environment and to determine the thermal characteristics of the material. The results of the initial screening to present are given in Table 1.

Table 1. Inorganic Samples Screened for Solubility

Significant weight change *	No Change, nothing extracted
NH_4HF_2 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ $\text{Fe}(\text{NH}_4)_2 \cdot 12\text{H}_2\text{O}$ $\text{Fe}(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Simulated Martian Regolith * Ten are hydrated species	CaCl_2 NaI AgNO_3 NH_4SO_4 $\text{K}_2\text{Cr}_2\text{O}_7$ $(\text{NH}_4)_2\text{MoO}_4$ CuCl_2 FeCl_3

Our data show that the only compounds which show any significant weight change are those who have associated with them water of hydration. It is therefore possible to recover water from hydrated species using supercritical carbon dioxide. Recovering water is significant, since water can be used to support life on Mars directly or the water can be broken down into hydrogen for fuel and oxygen for breathing or as an oxidizer. We are currently testing the water samples after extraction in the exit tube using ICP instrument to determine if there are any dissolve metal species in the solutions. Some visual evidence indicated by a reddish color in the water indicates we extracted iron.

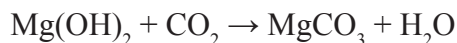
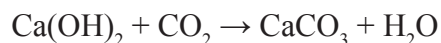
We have focused on recovering water of hydration from several of the species tested. Figure 5 shows the water recovered from three compounds we have tested. We did further testing of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to determine the temperatures at which waters of hydration are removed. Figure 6 is a TGA of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ sample. Table 2 shows the dehydration steps and our data and data from the literature for the removal of water at different temperatures.

Table 2. Dehydration Step Temperatures

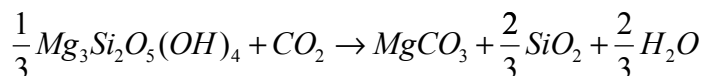
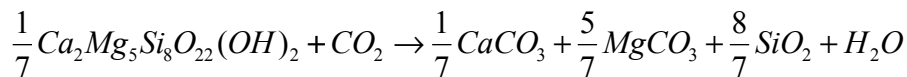
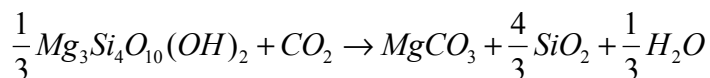
Dehydration Step	TGA Temperature Range	DSC Temperature Range	Literature Temperature Range (1)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow \text{FeSO}_4 \cdot 4\text{H}_2\text{O} + 3\text{H}_2\text{O}$	40-70 C	70-80 C	70-80 C
$\text{FeSO}_4 \cdot 4\text{H}_2\text{O} \rightarrow \text{FeSO}_4 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$	100-150 C	100-150 C	100-150 C
$\text{FeSO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{FeSO}_4 + \text{H}_2\text{O}$		250-300 C	300-350 C

Our data and the literature data are in close agreement. The first three waters are removed over the temperature range of 50-70 C, the next three between 110°C and 120°C, and the last water at around 300 C. Figure 7 shows a comparison between the water removed from just heating the sample at different temperatures up to 140 C and extracting samples in SC-CO₂. At all temperatures there is an enhancement due to SC extraction, which ranges from 4 to 9%. To estimate the bond energy, we performed a DSC on a fresh sample of FeSO₄•7H₂O. A typical scan is shown in Figure 8. We used different heating rates from 1 to 10 C/min to resolve the peaks which indicate the temperature at which the water bonds are broken. The area under the first peak at about 70 C corresponds to the energy required to release 3 waters. The energy required to break these bonds is about 44 J/g of water. At about 110 C there is a double peak. The area under the first of these peaks corresponds to energy to release the next three waters, approximately 283 J/g. The area under the second peak corresponds to the latent heat of vaporization of water at 121.5 C, approximately 2177 J/g. The table on the figure shows the literature value (2) for the heat of vaporization to be 2198 J/g, which agrees closely with the experimental data. The two peaks at about 300 C can be interpreted similarly. We have devised a method, which allows us to take our extracted samples from the extractor and examine them via DSC without re-exposing the sample to the atmosphere and allowing it to absorb water from the air. We are in the process of testing extracted samples. The results should tell which waters are being extracted.

Another possible path to water would be through the reactions of calcium hydroxide or magnesium hydroxide with supercritical carbon dioxide according to the following reactions:



The carbonate species are favored over the hydroxides. No evidence exists for the presence of hydroxides in the Martian soils although the recent Mars Odyssey data indicate the presence of hydrogen in a chemically or physically bound form. A more likely source of hydrogen would be in species such as Talc, Tremolite (Amphibole), or Chrysotile (Serpentine). The more complex crystal structures are more likely to trap the hydrogen molecules. Water can be released by reaction with supercritical carbon dioxide according to the following reactions.



We have initiated a set of experiments to include the reaction of these species at supercritical carbon dioxide conditions. Figure 9 shows the result of an experiment using serpentine with SC-CO₂. We believe this is an extraction and not a reaction. If a reaction was occurring, the sample should gain weight, not lose

it as a result of the reaction with CO_2 . We are continuing to study the serpentine, since reaction with SC- CO_2 holds the prospect of obtaining water. Different starting carbonation solutions including water and bi-carbonate solutions are being examined. To aid in identification of water, we have obtained an infrared gas-sampling cell to collect samples of extract in the sample cell before washing the CO_2 gas in water. The infrared analysis will aid in quantifying the water entering the supercritical CO_2 .

We are in the preliminary stages of modeling the solubilities in SC CO_2 . Our initial efforts to model the solubility of water in SC CO_2 have been a collaborative effort with Prof. G. Mauer, who has used molecular simulations to estimate these solubilities. These results, compared to the experimental data of Takenouchi and Kennedy are shown in Figure. 10.

We hope to extend the capability to extract metals and minerals from Martian soil with supercritical CO_2 by *using nano-sized-emulsion droplets of water in SC- CO_2 to extract mineral material from Martian surface soils and its igneous crust.* We will also continue to pursue the recovery of water from hydrated species and to produce water by reaction of SC- CO_2 with hydroxylated compounds such as serpentine.

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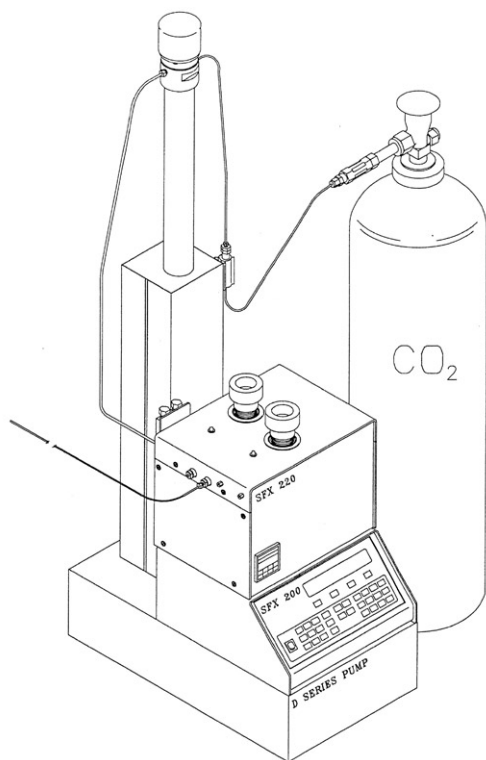


Figure 1. Supercritical fluid extractor.

Figure 2. Percent weight removed VS pressure at different temperature

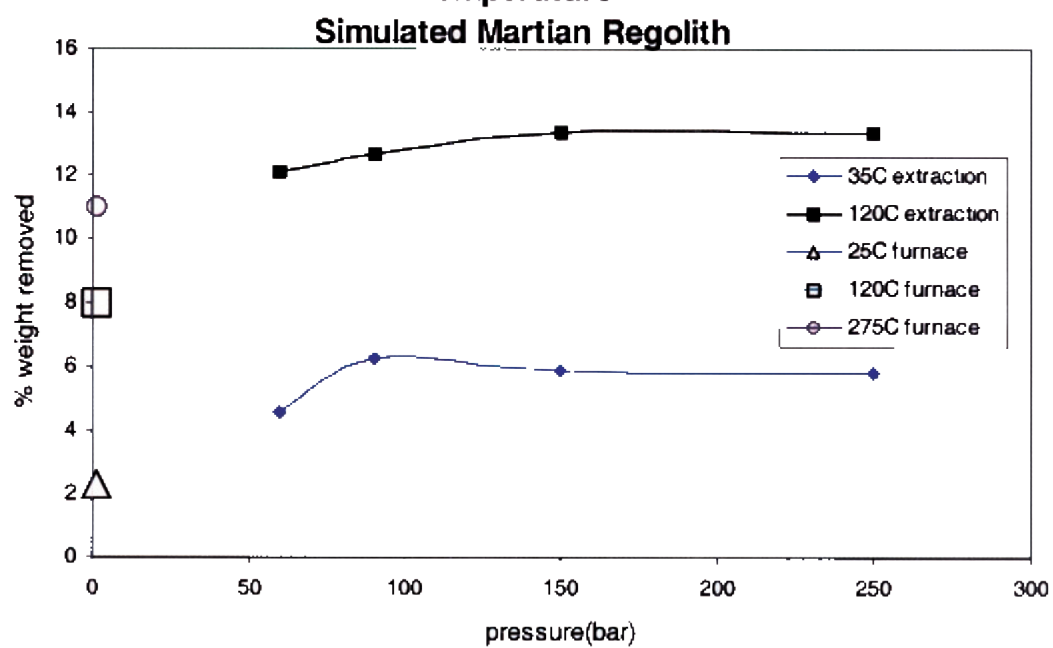


Figure 3. TGA for Simulated Martian Regolith

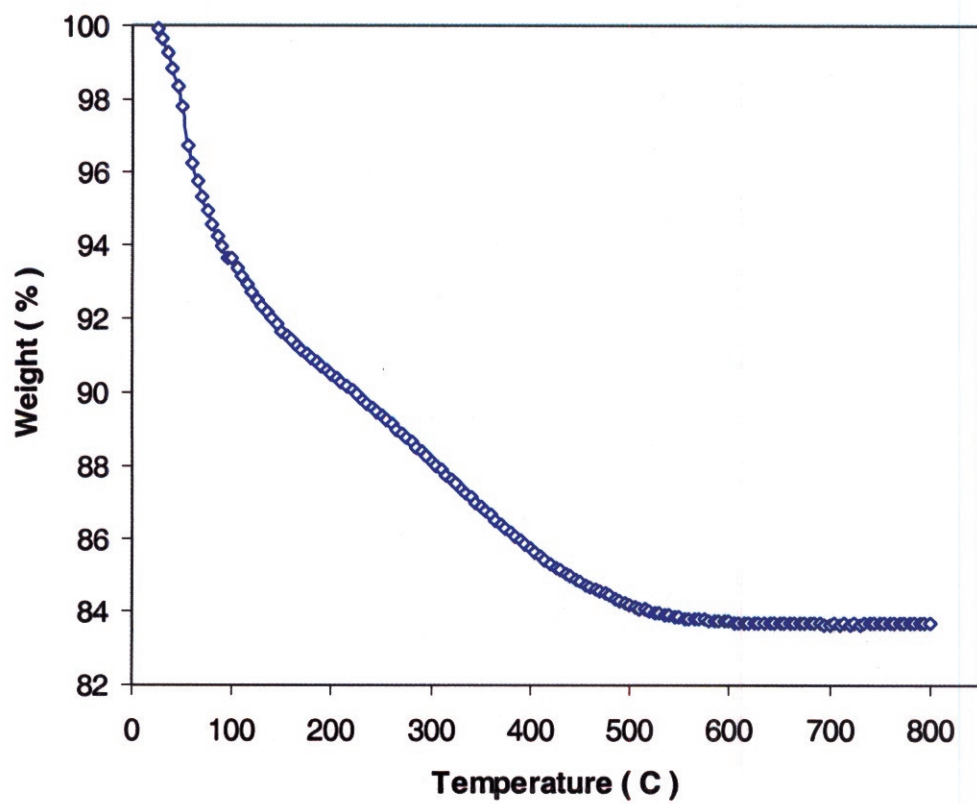
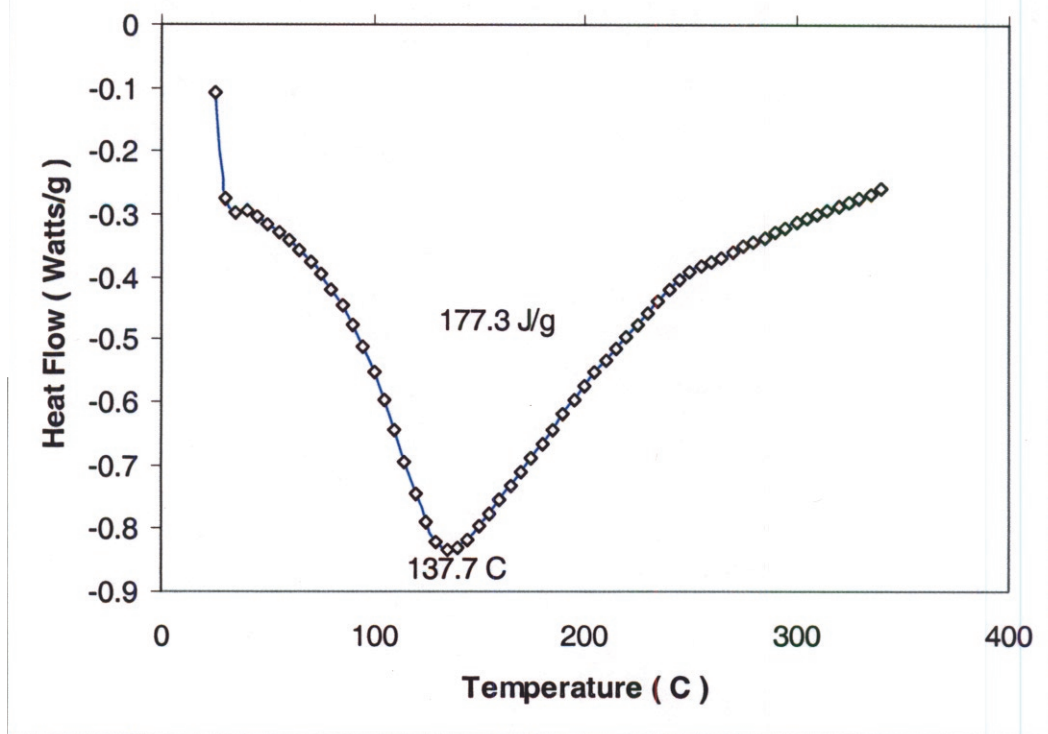
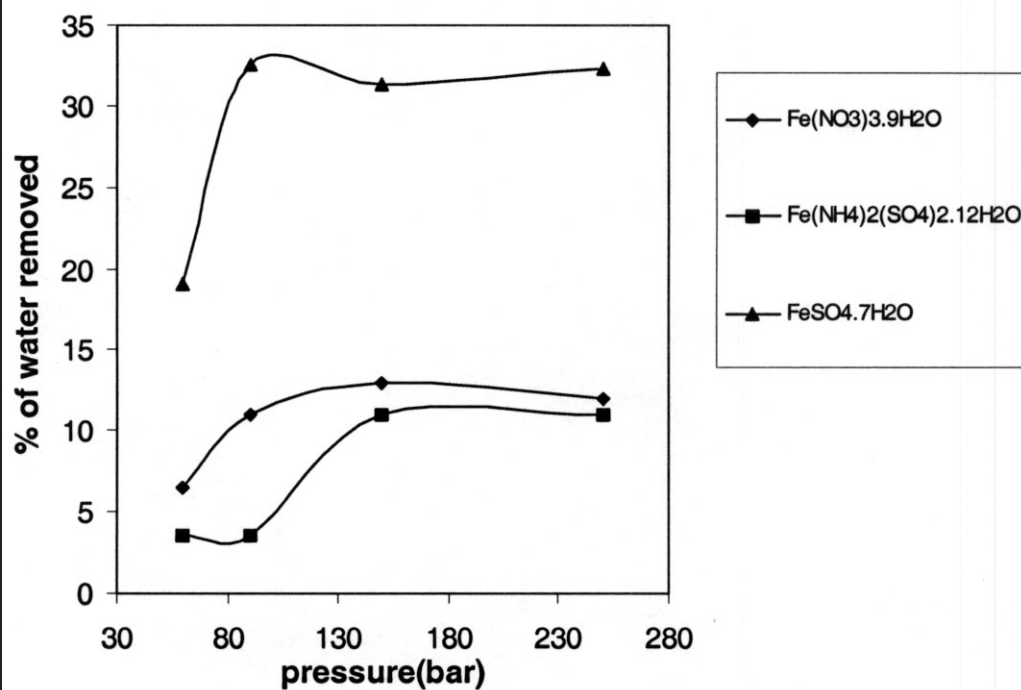


Figure 4. DSC for Simulated Martian Regolith



**Figure 5. Percent of water loss VS pressure
(35C, CO2 extraction)**



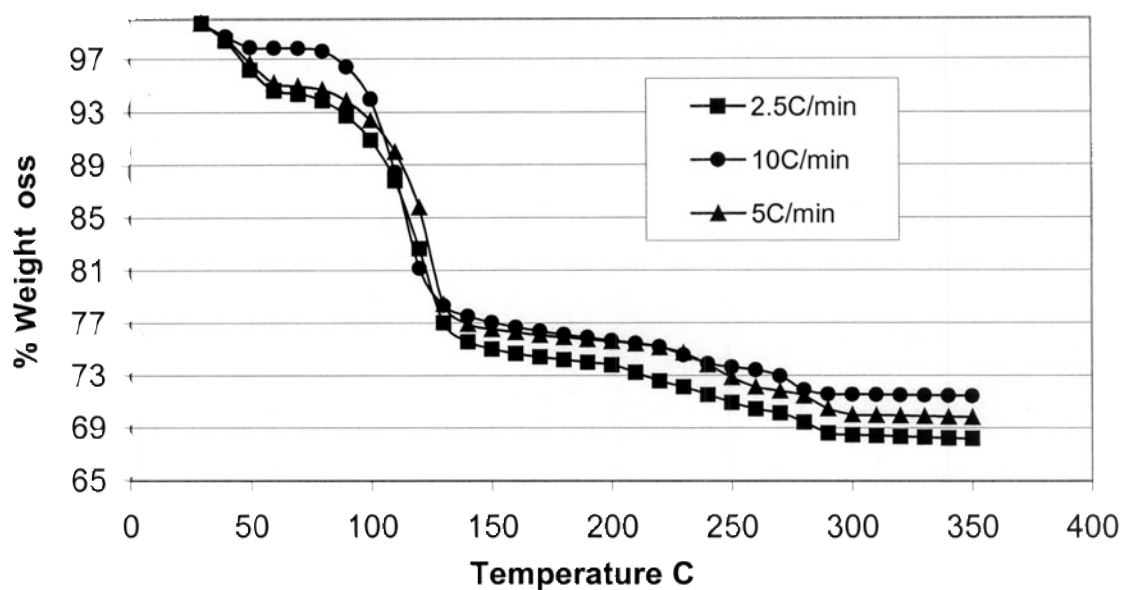


Figure 6 TGA of ferrous sulfate in non-isothermal conditions with different heating rate by using a nitrogen atmosphere

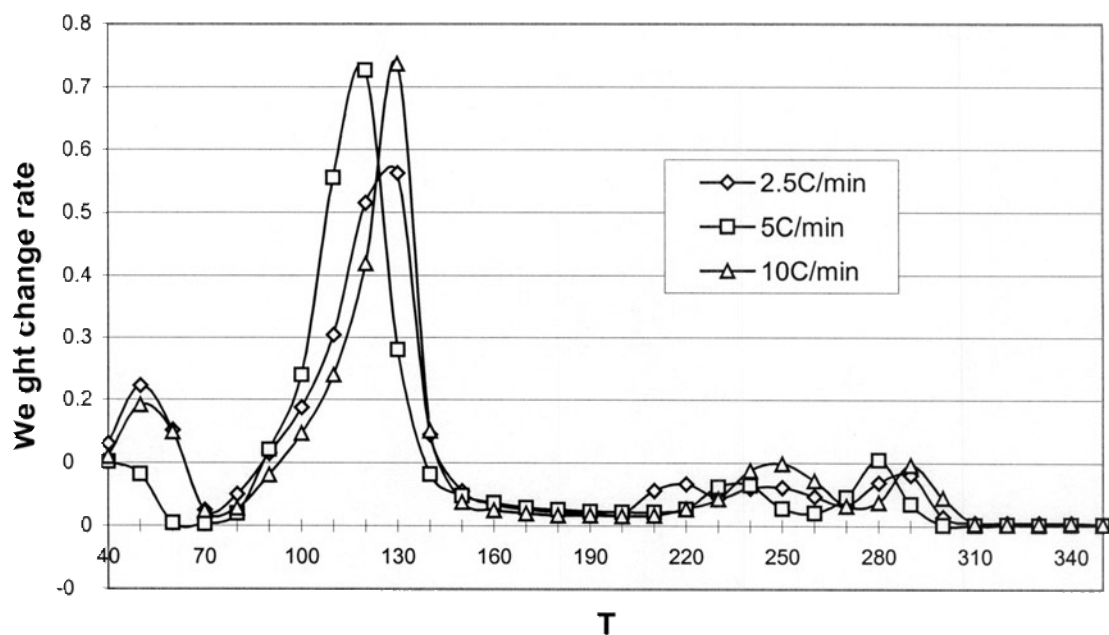
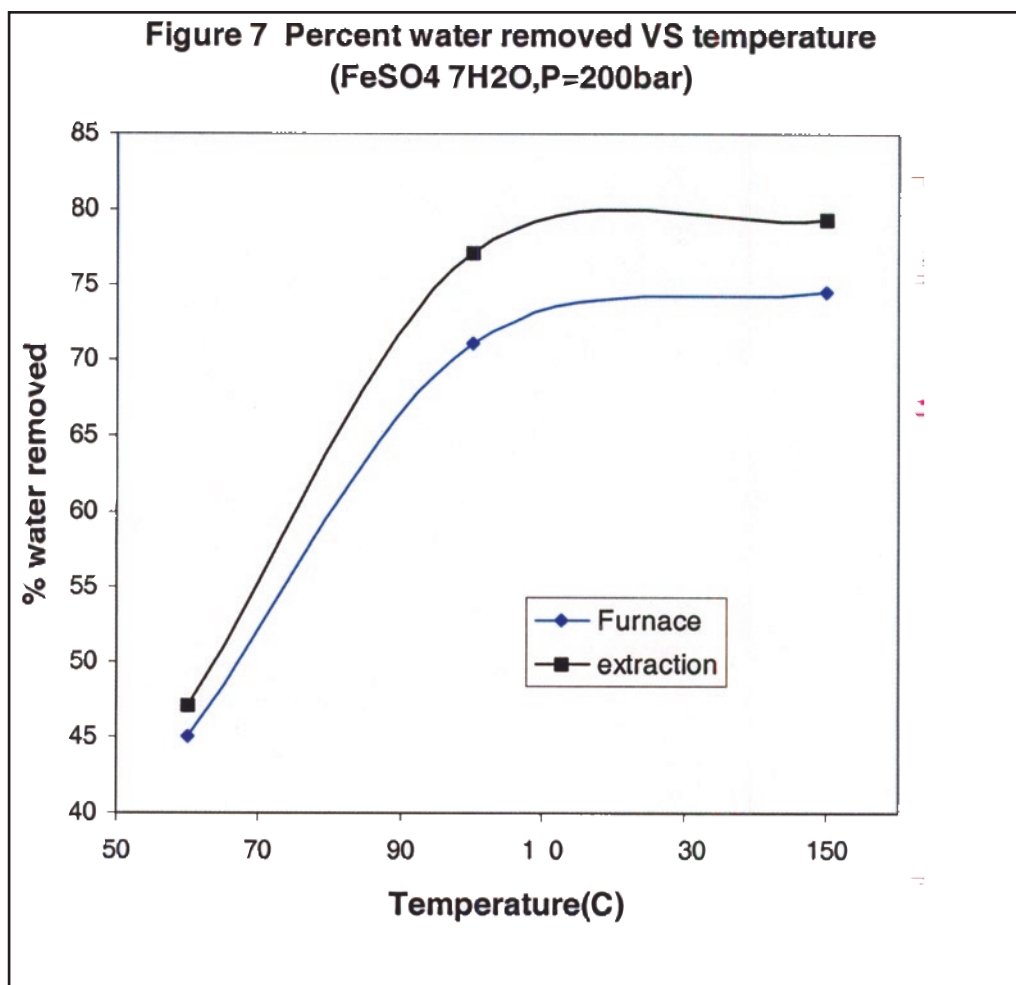


Figure 6a Weight loss rate with temperature of ferrous sulfate



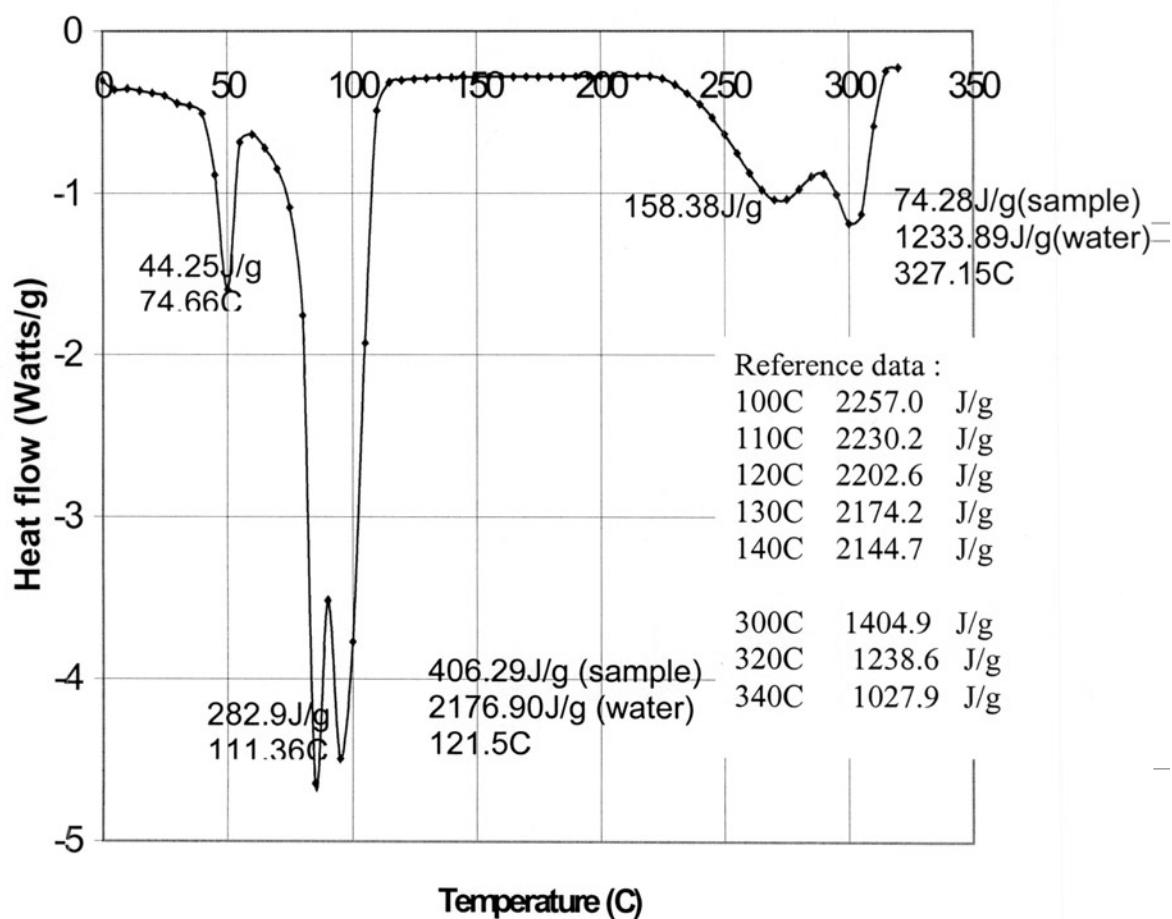


Figure 8: DSC of Ferric Sulfate at 10cpm

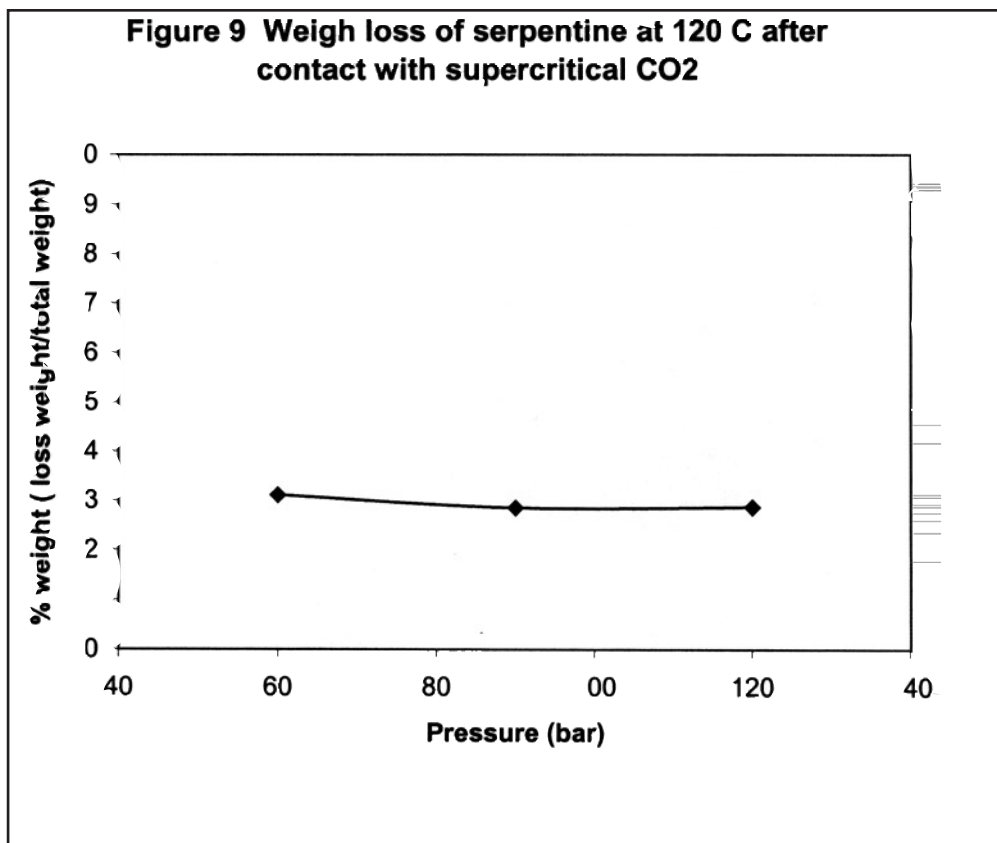
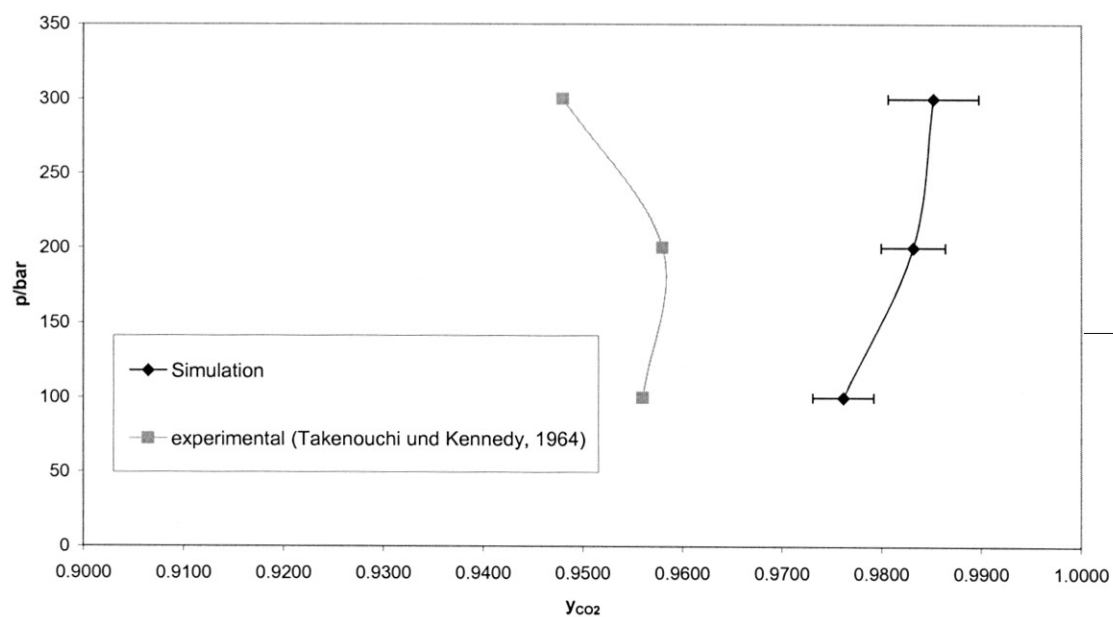


Figure 10. Comparison of Water Solubility in Supercritical Carbon Dioxide. Molecular Simulation and Experimental Data



MODELING THREE-DIMENSIONAL FLOWS AND G-JITTER DURING MICROGRAVITY BRIDGMAN GROWTH

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Buoyancy-driven melt convection dominates mass transport in many crystal growth systems, thereby having a critical effect on solute segregation. Since segregation in turn plays a key role in determining the properties of grown materials, there is widespread interest in the application of various methods to modify or suppress convection. In this vein, microgravity crystal growth promises great benefits for better understanding and control of buoyant flow. However, even small changes in acceleration (i.e., g-jitter) can drive flows significant enough to affect segregation.

We present an overview of a new finite element model for the parallel computation of three-dimensional flows, segregation, and solidification during Bridgman crystal growth. The model features a self-consistent coupling between the field phenomena (fluid flow, heat and mass transfer) and interfacial effects (solidification) via front-tracking techniques. Also of note is a new coupling with a sophisticated furnace model, the CrysVUN++ code of Mueller et al., to provide realistic heat transfer boundary conditions.

We present initial results for several three-dimensional systems, including an ground-based horizontal Bridgman system and a prototype system for microgravity and g-jitter.

Keywords: 3-D modeling, segregation, g-jitter, convection, finite element method, theoretical

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FIRST PRINCIPLES CALCULATIONS OF LIQUID II-VI COMPOUNDS AT TEMPERATURES ABOVE AND BELOW THEIR MELTING POINTS

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This presentation will highlight results obtained from quantum mechanical molecular dynamics simulations of the liquid state of several II-VI tellurium-containing compounds, notably CdTe and ZnTe. These materials are employed in a variety of technologically important electronic and electro-optical devices; however, their growth has typically proven to be extremely difficult. We seek to obtain a more fundamental understanding of the properties of these compounds so that the physical mechanisms responsible for growth can be elucidated.

Our simulations use the pseudopotential density functional method (PDFM) to calculate quantum forces in the melt. We prepare a liquid state ensemble using supercells and Langevin dynamics to thermalize the liquid. One of the most interesting issues in these materials concerns the conductivity of the liquid state. Most Group IV and III-VI semiconductors are metallic in the liquid state; however, some II-VI semiconductors remain semiconducting in the melt. In order to examine this problem in more detail, we have calculated the conductivity of a prototypical III-V semiconductor (GaAs) and compared its properties to II-VI semiconductors. Our demonstration illustrates the microstructure of the liquid state and the self-diffusion of different species within the melt. We will also discuss why it may be difficult to grow Te-containing II-VI's from the melt.

Keywords: II-VI compounds, atomistic computations, molecular dynamics, pseudopotentials, theoretical

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REAL-TIME OPTICAL MONITORING AND SIMULATIONS OF GAS PHASE KINETICS IN InN VAPOR PHASE EPITAXY AT HIGH PRESSURE

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Abstract

Understanding the kinetics of nucleation and coalescence of heteroepitaxial thin films is a crucial step in controlling a chemical vapor deposition process, since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. The initial nucleation process also defines the film quality during the later stages of film growth. The growth of emerging new materials heterostructures such as InN or In-rich $\text{Ga}_x\text{In}_{1-x}\text{N}$ require deposition methods operating at higher vapor densities due to the high thermal decomposition pressure in these materials. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition or etching experiments. Because of the difficulty with maintaining stoichiometry at elevated temperature, current knowledge regarding thermodynamic data for InN, e.g., its melting point, temperature-dependent heat capacity, heat and entropy of formation are known with far less accuracy than for InP, InAs and InSb. Also, no information exists regarding the partial pressures of nitrogen and phosphorus along the liquidus surfaces of mixed-anion alloys of InN, of which the $\text{InN}_x\text{P}_{1-x}$ system is the most interesting option. A miscibility gap is expected for $\text{InN}_x\text{P}_{1-x}$ pseudobinary solidus compositions, but its extent is not established at this point by experimental studies under near equilibrium conditions. The extension of chemical vapor deposition to elevated pressure is also necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures.

Introduction

In this paper we describe our progress in establishing a high-pressure chemical vapor deposition (HPCVD) system with integrated real-time optical monitoring capabilities[1-3]. The objective of this work is the real-time evaluation of the growth kinetics of nucleation and coalescence of heteroepitaxial thin films, which is an important step of chemical vapor deposition since it defines the perfection of the heteroepitaxial film both in terms of extended defect formation and chemical integrity of the interface. Presently, most growth efforts focus on low pressure processing to minimize the influence of flow dynamics on process uniformity and favors for III-V compounds organometallic chemical vapor deposition (OMCVD). However, the extension to above atmospheric pressures is necessary for retaining stoichiometric single phase surface composition for materials that are characterized by large thermal decomposition pressures at optimum processing temperatures. For example, $\text{Ga}_x\text{In}_{1-x}\text{N}$ heterostructures have been identified as an important basis for manufacturing of optoelectronic and microelectronic devices, such as, light sources, detectors and high power microwave devices for which large potential markets can be identified. Due to the high

Keywords: real-time monitoring, high-pressure CVD, gas phase kinetics, thin film epitaxy, new research

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thermal decomposition pressure of InN, these devices are at present limited to gallium-rich compositions. High nitrogen pressure has been demonstrated to suppress thermal decomposition of InN, but has not been applied yet in chemical vapor deposition or etching experiments. Because of the difficulty with maintaining stoichiometry at elevated temperature, current knowledge regarding thermodynamic data for InN, e.g., its melting point, temperature-dependent heat capacity, heat and entropy of formation are known with far less accuracy than for InP, InAs and InSb. Gaining access to these data will require the development of new real-time optical diagnostics, capable to obtain sufficient accurate data on flow conditions, gas phase reactions as well as on the surface reaction kinetic to support modeling and simulations of thin film growth under laminar and/or turbulent flow conditions at sub-atmospheric pressure.

The here-presented research focuses on the base material InN and addresses both: (a) the prediction and simulation of gas phase reactions and surface kinetics of InN growth at high pressures (up to 100 bar) and (b) real-time optical monitoring of gas phase- and surface chemistry processes during high pressure chemical vapor deposition (CVD) of InN. We describe the present status of our modeling and simulations efforts on gas phase and surface reactions kinetics for InN growth at high pressures, which is based on a numerical solution of nonlinear, coupled partial differential equations representing the conservation of momentum, energy and total mass as well as balances over the individual species involved in the InN deposition. The operating conditions modeled correspond to flow dominated by forced convection where $Gr \ll Re^2$. We also describe the capabilities of the implemented high-pressure CVD reactor and the real-time optical monitoring techniques available in this reactor.

High-pressure Reactor

The growth of III-nitrides under HPCVD conditions with integrated optical diagnostics requires a complete new reactor design as well as new gas mixing and gas injection controls. Figure 1a) depicts a side view of the assembled HPCVD reactor with flow direction from right to left. The flow control panel depicted in Figure 1b) is fully computer interfaced and provides:

- the compression of the III- and V-gas sources ($\leq 100\text{bar}$),
- the mixing of the gas sources and dilution of the gases in nitrogen carrier gas,
- the pulsed injection of all gas sources,
- the pressure control of the reactor in the pressure range of 1 to 100 bar.

The flow channel of HPCVD reactor has constant cross section from entrance to the exit with symmetric sapphire substrates arrangements in the upper and lower channel walls. Details in the design were reported previously[3]. Thus the bifurcation of nutrient fluxes to the top and bottom channel walls is symmetric to the center-line. Thus well behaved flow and deposition can be expected in the targeted pressure range. Pressure tests were performed up to 120 bar with flows from 10 slm to 50 slm. In the next step we interfaced the reactor to the gas injection panel shown in Figure 1b. The gas injection sequences are presently tested and optimize in timing and flows. An exact timing is not only important to avoid pressure fluctuations during the switching sequences, but also to synchronize the gas precursor injection with the optical monitoring techniques.

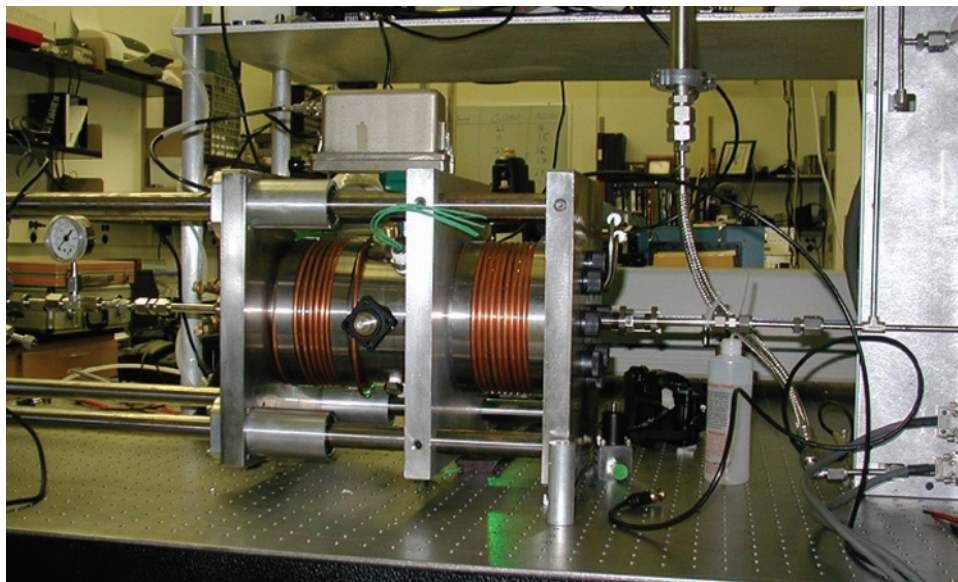


Figure 1a. Side view of the completely assembled HPCVD reactor with gas injection from the right. The optical monitoring plane is in the center of the substrates.

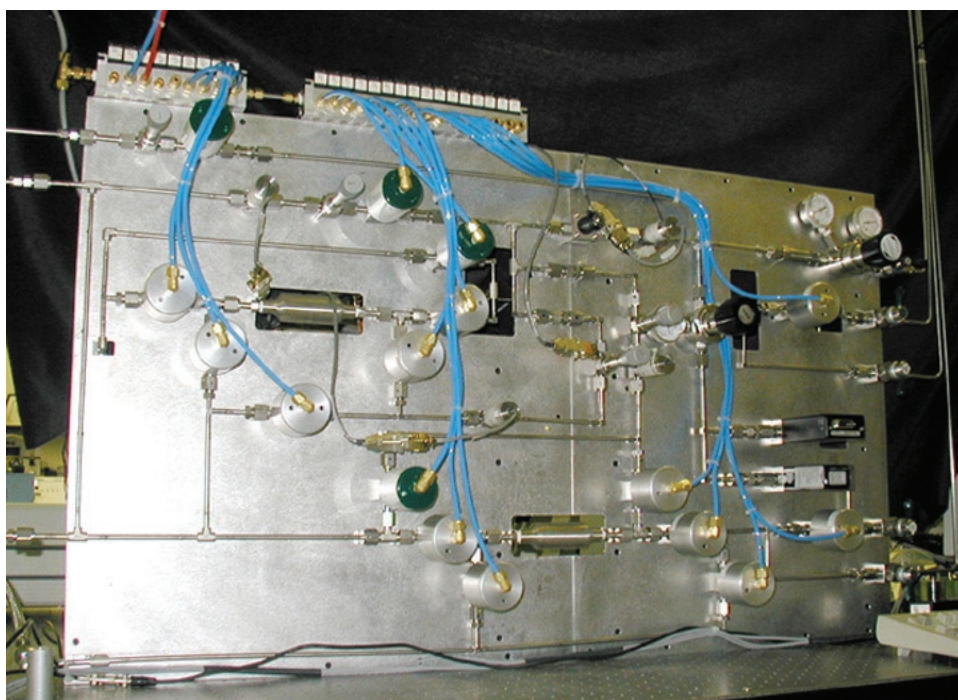


Figure 1b. Flow control panel for precursor compression and pulsed precursor gas injection.

For real-time gas flow dynamics studies as well as the analysis of the gas-phase decomposition kinetics during the thin film growth process, we integrated optical access ports in the reactor as schematically shown in Figure 2. The access ports allow the optical monitoring perpendicular to the flow direction at the center line of the two symmetric in the upper and lower channel walls inserted substrates. Two optical ports provide access to flow channel and allow the monitoring of gas flow and gas-phase decomposition kinetics. As depicted in Figure 3a, three ports in each half of the symmetric reactor provide access through the backside of the substrate to the growth surface and with it to the growth process itself. The optical rods

are made of sapphire and with its refractive index matched to the sapphire substrates. The rods are inserted through the outer reactor shell in the inner shell and touch the substrates from the back. The pressure is retained by a double o-ring seal within the outer reactor shell. A protective cap on the outer side of the holder prevents the rod from moving outwards.

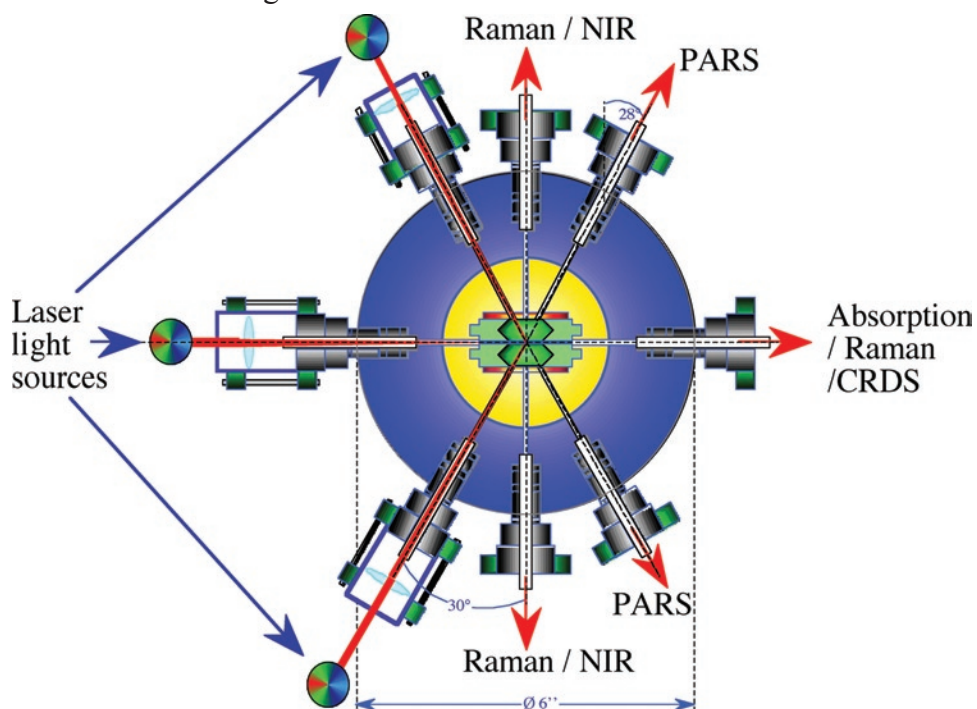


Figure 2. Cross Section of HPCVD reactor, which contains the integrated optical access ports. The cut is perpendicular to the flow channel.

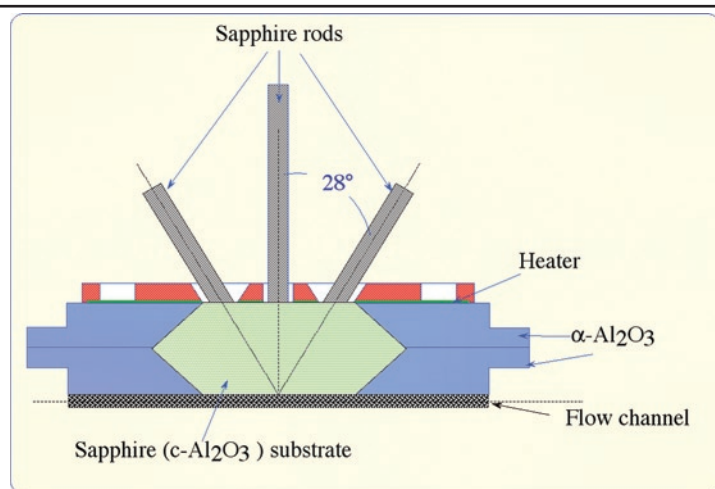


Figure 3a. Optical access rods to monitor the growth process through the backside of the substrates.

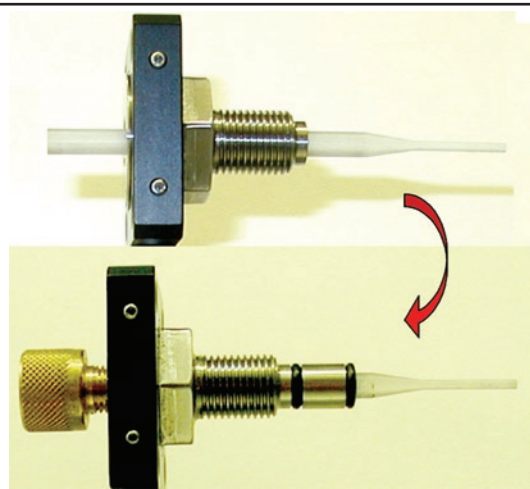


Figure 3b. Double O-ring sealed sapphire rod assembly before inserting in reactor.

The optical real-time monitoring capabilities will provide crucial experimental data as they are entering as input parameter for process models and simulation codes as well as to establish growth parameter sets needed for analysis and control of chemical vapor deposition at elevated pressure. Access to a microgravity environment will allow to retain laminar flow at high pressure conditions, which is essential

for successful acquisition and interpretation of the optical data. In the following, we present our modeling and simulations efforts on gas phase and surface reactions kinetics for InN growth at high pressures.

Modeling and Simulations

The HPCVD reactor simulations are based on a numerical solution of nonlinear, coupled partial differential equations representing the conservation of momentum, energy and total mass as well as balances over the individual species. The modeling equations were solved using the finite volume element method based upon an integral form of the equations to be solved. The integration of the differential equations leads to a set of algebraic equations which are solved internally by the CFD-ACE(U) iterative, segregated solution method wherein the equation sets for each variable are solved sequentially and repeatedly until a converged solution is obtained. The operating conditions correspond to flow dominated by forced convection where $Gr \ll Re^2$. Details on the boundary conditions are given elsewhere[4]

The surface reaction mechanism for growth of InN has been described by a reduced-order model, noting that a larger number of possible reactions may have to be taken in account[5-7]. The reduced order model is based on pulsed chemical vapor deposition, which substantially reduces the number of reacting species. A typically precursor injection sequence is depicted in Figure 4. The V/III ratio has to be chosen properly to assure the incorporation of In-atoms supplied to the surface into the InN lattice. The assumed surface reactions are summarized in Table 1, showing the adsorption of the reactive species that are present in the gas phase, with rate parameters given by Cardelino et al.[8]. The growth of InN from trimethylindium (TMI) and ammonia (NH_3) has been simulated based on the reduced-order model, with flow, heat and mass transfer in the HPCVD reactor evaluated for a symmetrical substrate wafers positioning.

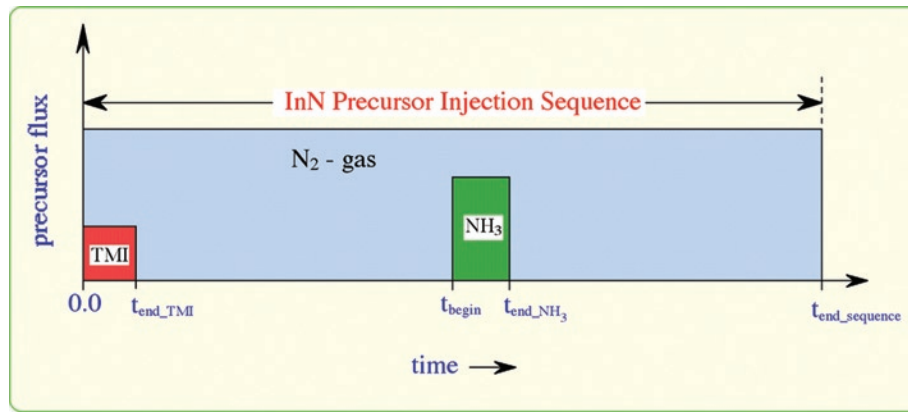


Figure 4. Schematic timing sequence for the precursor injection for InN growth.

The gas phase reactions of TMI according to Table 1 were obtained in the pressure range of 10 to 100 atm as a function of substrate temperature and centerline flow velocity under steady-state conditions. The predicted gas phase reaction variations with centerline flow velocity for $p = 100$ atm and $T_s = 900$ K are depicted in Figure 5. The simulations show the vapor phase concentration of MMI at the gas - substrate interface with $p = 100$ atm, $u = 12$ slm and $T_s = 900$ K and with $p = 10$ atm, $u = 60$ slm and $T_s = 900$ K, in Figures 5a and 5b, respectively. A comparison shows that for $u = 12$ slm and $p = 10$ atm the maximum concentration of MMI is at the center of the substrate (see Figure 5a), whereas for $u = 60$ slm and $p = 10$ atm, the maximum concentration of MMI has shifted downstream. The simulations indicate that for higher centerline velocities the maximum concentration of MMI will shift downstream, which would prevent the maximum MMI flux to become adsorbed at the center of the substrate. When the flow rates

increased to 120 slm at $p = 10$ atm and $T_s = 900$ K, the Re number equals 3000, which requires the use of the k-epsilon model to account for the effects of turbulence.

Table 1. Reduced-Order Model: Pulsed TMI followed by Pulsed NH_3

Gas Phase Reactions:	$\text{TMI(g)} \rightarrow \text{DMI(g)} + \text{CH}_3$
	$\text{DMI(g)} \rightarrow \text{MMI(g)} + \text{CH}_3$
	$\text{NH}_3(\text{g}) + h\nu (170\text{-}220 \text{ nm}) \rightarrow \text{NH(g)} + \text{H}_2$
Surface Reactions:	$\text{MMI(g)} + \text{S}_1 \rightarrow \text{MMI}_{\text{ad}}$
	$\text{NH(g)} + \text{MMI}_{\text{ad}} \rightarrow (\text{HN:MMI})_{\text{ad}} \rightarrow \text{InN(s)} + \text{CH}_4 \uparrow$

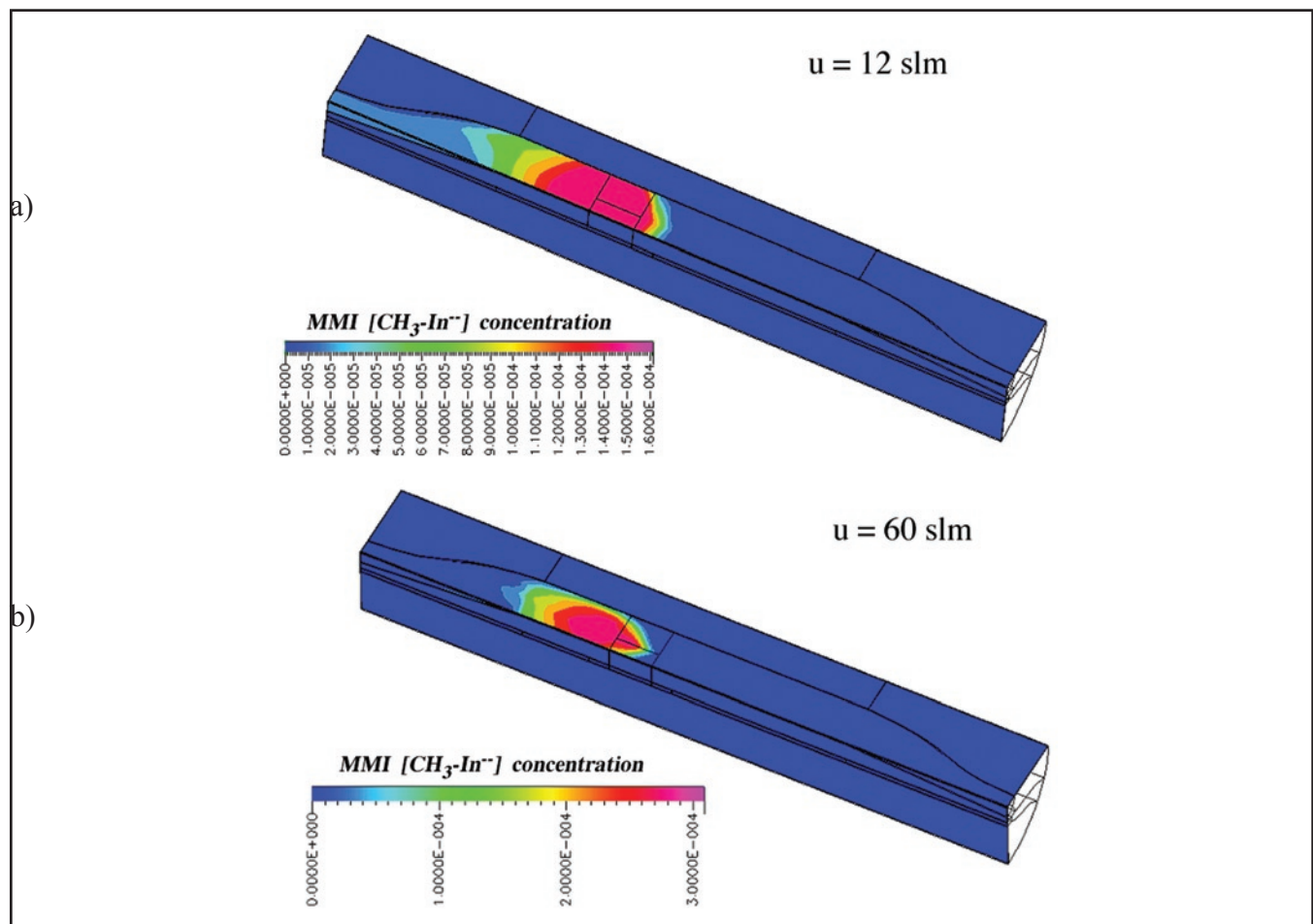


Figure 5. Effect of Centerline flow velocity for $P = 100$ atm and $T_s = 900$ K.

At the optimum growth temperature of $T_s = 900$ K in the pressure range of 10 to 20 atm, the concentration of MMI and atomic indium is evenly distributed over the substrate surface as seen in Figures 6 (a-d), respectively. The effect of the increasing pressure on the gas phase kinetics is summarized in Figure 7 for a substrate temperature of 1000K and a centerline velocity $u=12$ slm.

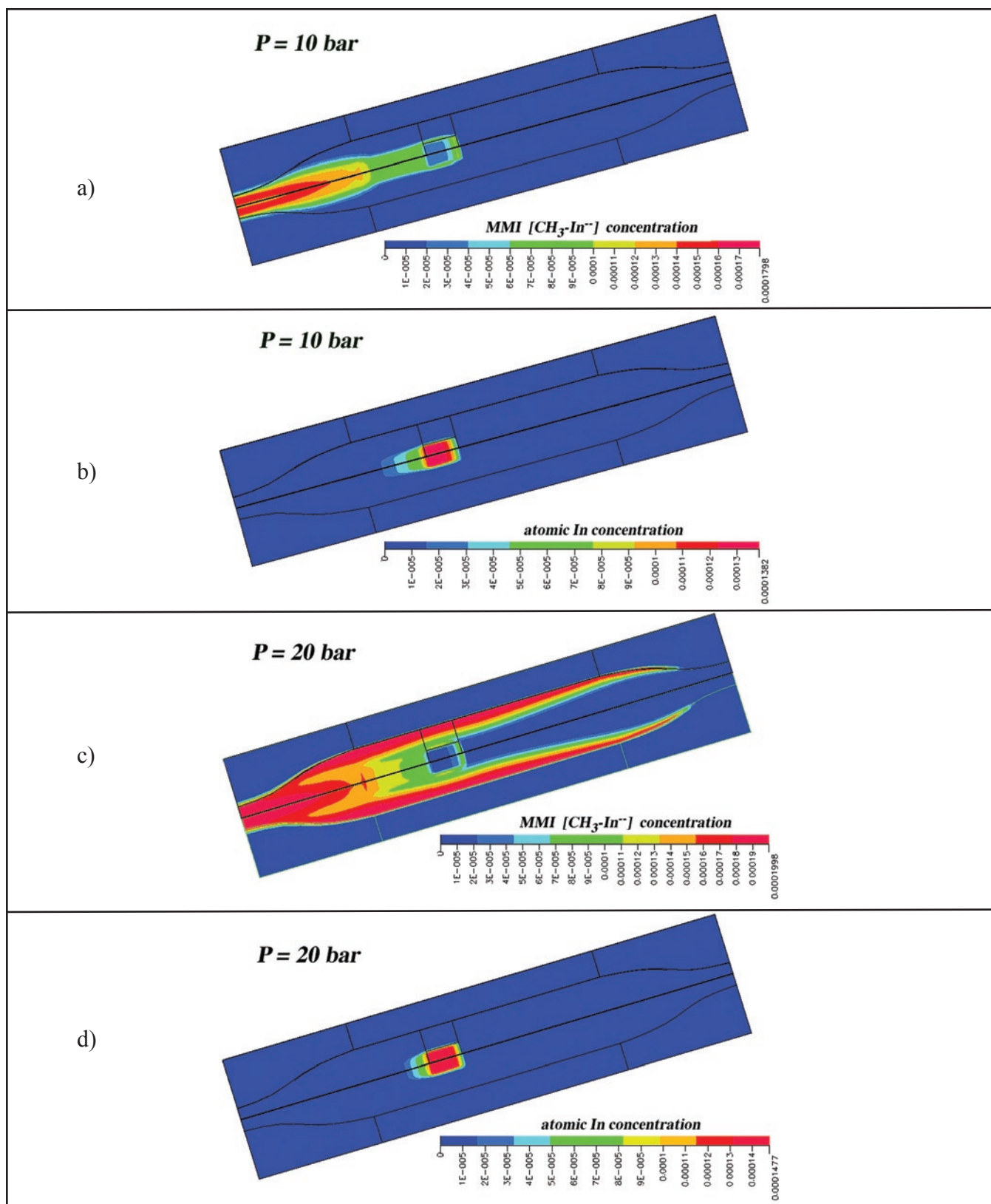


Figure 6. Trimethylindium (TMI) gas phase decomposition in monomethylindium (MMI) and atomic indium at 10 and 20 bar at a substrate temperature of 1000 K and a flow of 12 slm.

The most dominate changes in the DMI, MMI and atomic indium concentrations are expected in the pressure range between 1 and 20 atm. As depicted in Figure 7, a further pressure increase beyond 40 bar does not significantly alter the MMI and atomic indium concentration at the center of the substrate, which is accessible for experimental validation. These results are in good agreements with ab initio calculations by Cardelino et al.[9], which show in inversion of monomethylindium versus atomic indium concentration in the pressure range of 1 bar to 20 bars.

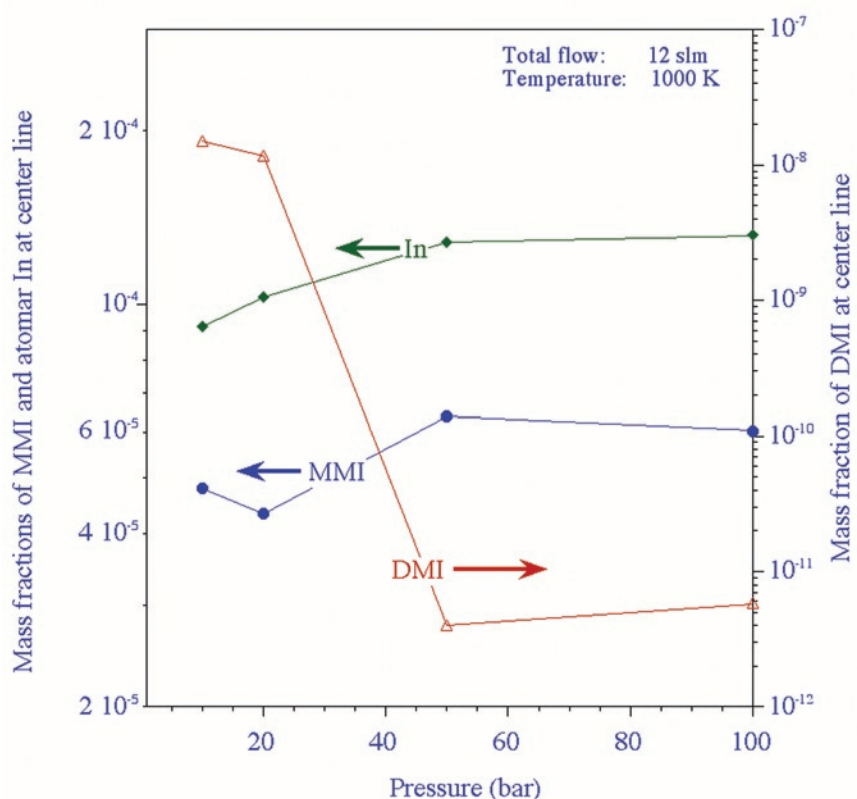


Figure 7. Effects of pressure on gas phase kinetics at $T_s = 1000\text{K}$ and $u = 12$ slm.

InN Growth Rate Simulations

A 2-dim, time-dependent simulation model was used to combine the gas phase reactions and transport with surface reactions leading to InN formation using a pulsing sequence as illustrated in Figure 4. The timing of the precursor injection keeps the process gases separate and thus precludes homogeneous formation and transport of adducts in the gas phase. The injection sequence introduces $\text{N}_2 + \text{TMI}$; N_2 ; $\text{N}_2 + \text{NH}_3$; N_2 . into the reactor flow channel with an experimental limit of approximate 0.2 seconds.

Figure 8a illustrates the site fraction of MMI adsorbed to the surface as a function of time. As shown in Figure 7, the surface of the substrate is completely covered by MMI until NH is introduced and InN is formed. This film growth begins when NH is generated and interacts with the MMI covered substrate. The results are tentative in that experimental work needs to be done to validate the mechanisms selected and preliminary reaction rates theoretically derived.

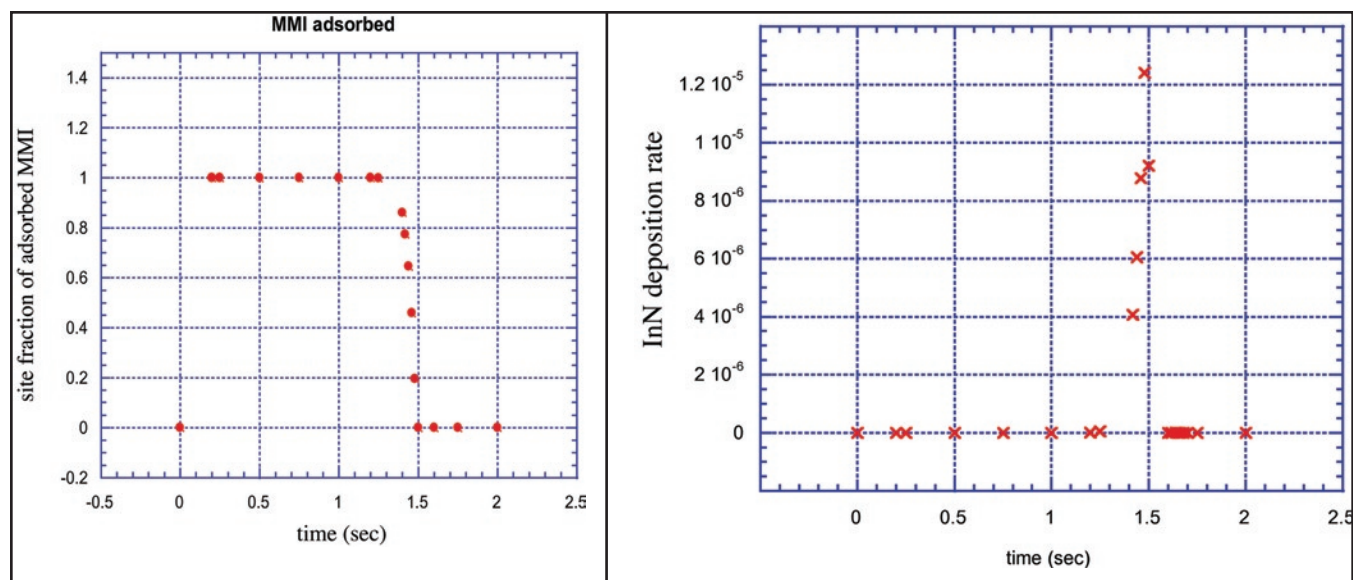


Figure 8. **a)** Site fraction of adsorbed MMI as a function of time. **b)** Deposition rate of InN vs. time at the center of the substrate.

Acknowledgments

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EXPERIMENTAL TECHNIQUE FOR THE STUDY OF HIGH-TEMPERATURE PHASE EQUILIBRIA IN REACTIVE MOLTEN METAL BASED SYSTEMS

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Introduction

The study of high-temperature phase equilibria in systems of metals with their respective oxides, nitrides, and carbides, such as Al-O-N, Mg-O, Zr-O-N, Ti-C-O-N, B-C-O, etc., is not straightforward. Increased reactivities at temperatures exceeding 1700 K cause reactions between samples and containers; compositions in systems with high vapor pressures such as magnesium metal or boron oxide become difficult to control. Phase equilibria as well as heterogeneous reaction kinetics are difficult to investigate directly at temperatures relevant for combustion processes (> 2500 K) where solid, liquid and gaseous phases are present, and gravitational effects become significant (convection, gravitational phase segregation).

At the same time, practical applications require reliable knowledge of phase equilibria in reactive, high temperature (molten) metal-based systems. Boron and aluminum based materials are routinely added to propellants or explosives to improve their combustion performance [1-3]. Zirconium oxides and oxynitrides are used at elevated temperatures as oxygen sensors [4], or in fuel cells [5]. Boron oxides and carbides find applications as semiconductors [6], glasses [7], and ultrahard materials [8] all of which require processing at high temperatures.

To deal with issues of sample containment, containerless experimental setups based on acoustic levitation were successfully used in the past [9-15]. This paper describes the adaptation of the acoustic levitation technique to microgravity in order to eliminate gravitational settling and convection effects for the study of phase equilibria in reactive molten metal based systems.

Experimental concept and constraints

The containerless microgravity experiments will be conducted aboard a NASA KC-135 aircraft flying parabolic trajectories. Single-axis acoustic levitation will be used to suspend samples in normal gravity, and primarily as a means to stabilize samples in microgravity. Samples will be prepared as pellets of premixed solid components, e.g., mixtures of ZrO_2 , ZrN, and Zr powders to study equilibria in the Zr-O-N system. Heating and equilibration of samples by laser radiation in an inert environment will be followed by splat-quenching and subsequent sample recovery for phase analysis. Phase analysis will be carried out using X-ray diffraction (XRD), and quantitative electron microscopy (SEM and TEM). In addition, ignition and combustion processes (or metal-oxygen interaction and equilibria) can be studied *in situ* in oxidizing environments.

The goal of this work is to design an experimental technique for high-temperature phase equilibrium studies that enables one to accomplish the following:

Keywords: containerless experiments, levitator, metal-oxide, metal-gas, phase equilibria, new research

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- a. Provide a controlled atmosphere;
- b. Position the sample before the KC-135 aircraft establishes microgravity conditions using an acoustic levitator;
- c. Heat the sample using a laser beam to a target temperature;
- d. Concurrently monitor radiation emitted by the sample;
- e. Quench, and recover the sample for further analysis.

Each aspect of the experimental technique will be described in detail below.

The time for equilibration in microgravity experiments is primarily constrained by the duration of a parabolic trajectory of the KC-135 aircraft during which microgravity is available (20-25 s). Consequently, sample sizes are limited to small amounts that can be heated and equilibrated in this time frame. Quench rates required to obtain samples representative of high temperatures further limit the amount of sample per experimental run.

Environmental control

The system for sample positioning, heating and quenching is enclosed in a chamber with transparent Lexan walls. During an experimental run, the chamber is hermetically sealed; it is dimensioned to withstand 2 atm positive pressure as well as 200 mm Hg vacuum. The moving parts of the assembly within the chamber (positioner, quencher) are controlled by electrically driven positioning systems, or from the outside via sealed feedthroughs.

Composition and pressure of the atmosphere in the chamber are adjusted prior to each experiment. Ports and gauges for pressure monitoring and post-experiment atmosphere sampling are provided.

Sample positioning

Figure 1 shows the sample positioning setup including the ultrasonic levitator and two protective wire mesh screens. The quenching mechanism is shown schematically. It includes brass blocks attached to aluminum arms—a more detailed description is given below.

The ultrasonic levitator is built on the basis of a 20 kHz Branson 900BC welding system. It consists of the following components: a piezo-electric transducer to generate the acoustic signal, a booster amplifying the oscillations, and a horn with a circular vibrating plate (actuator, 5.1 cm diameter) that produces a focused and directed acoustic field. A concave circular reflector (7.5 cm diameter) is placed coaxially to the horn. The concave shape of the reflector enhances the levitation forces [16,17] acting on the sample by creating radial forces acting towards the axis of the cylindrical space between horn and reflector. The distance between the radiator plate and the reflector is adjustable from 3 to 15 cm.

Two wire mesh screens are placed above and below the levitating sample to protect the reflector and the actuator from potential damage caused by accidental contact with the molten sample. These screens are mounted on linear slides and are also used for initial positioning of the sample inside the chamber. Prior to the experiment, the screens are brought close together to hold a sample pellet between them. The initial location of the sample, or the coordinate where the wire mesh screens meet, is selected to be close to the location of a pressure node in the standing acoustic wave (see below). The sample is held by the screens when the chamber is closed and the acoustic field is turned on. After a standing acoustic wave is established

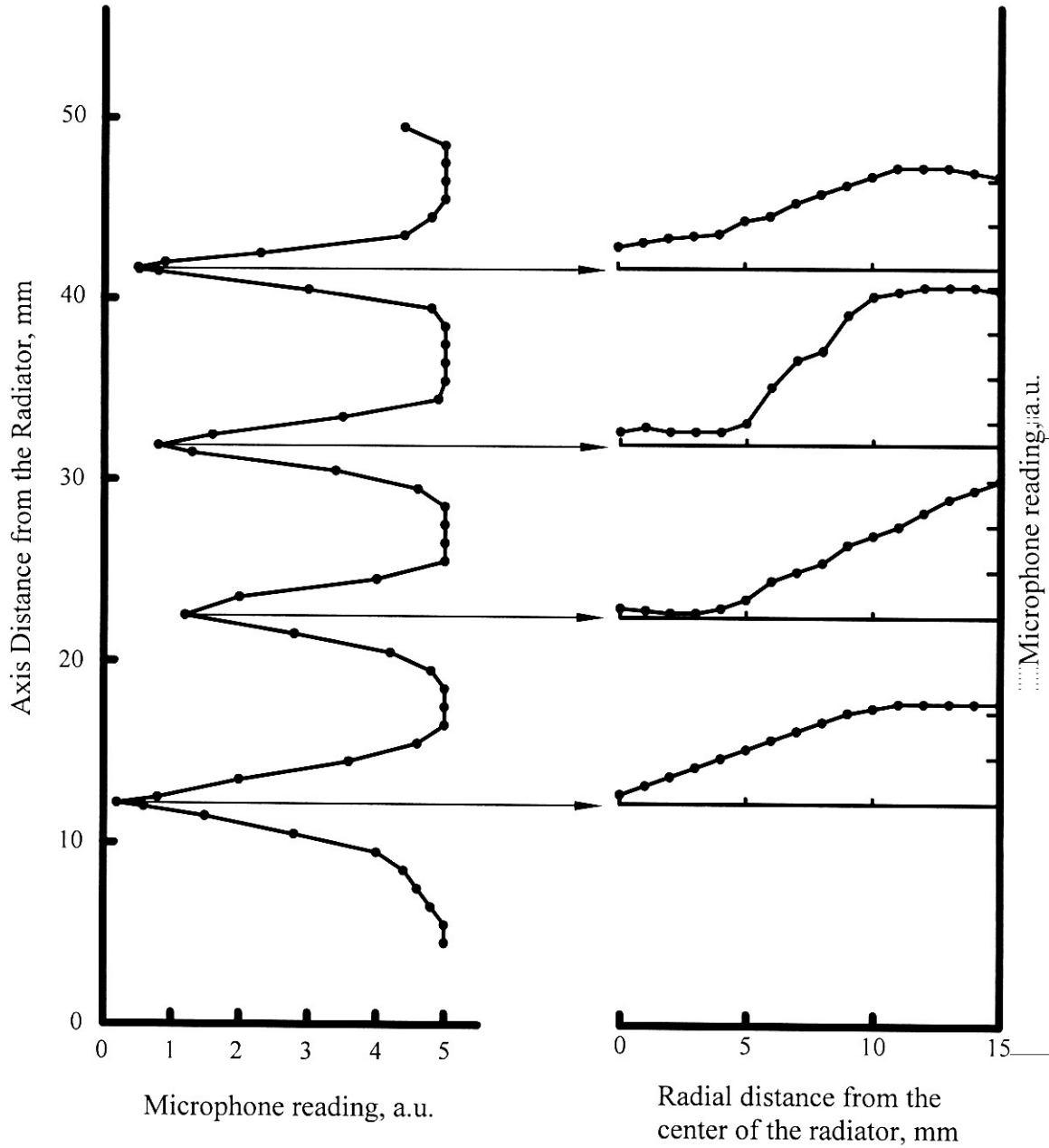


Fig. 2: Axial and radial pressure distribution in the acoustic field between radiator and reflector.

A flat reflector and two concave reflectors with curvature radii of 50 cm and 30 cm were tested to select the optimum configuration. Fig. 2 shows the results of the measurements for one of the resonance conditions (56.4 mm between radiator and reflector) using the reflector with a curvature radius of 30 cm. The axial pressure profile as well as the radial pressure profiles for each node are shown separately. The deepest pressure minimum is observed at the nodal point located near the radiating surface, at a distance from the actuator of 12.2 mm (about 3/4 of the acoustic wavelength for air at 20 kHz). The pressure gradient in both axial and radial direction is quite steep, so it is reasonable to expect that samples can be levitated readily at this location. However, the close proximity to the actuator makes the use of this node undesirable because of limited space, e.g., for sample quenching and somewhat inconvenient initial sample positioning. In addition,

the heat transfer from the molten sample to the actuator could be significant and could cause damage to the acoustic levitation system. Among the other nodes, the third node (at 31.9 mm) appears as an acceptable alternative because of the combination of the relatively low pressure and high axial and radial pressure gradients.

The final choice of the location for the sample levitation was made both, based on the microphone readings (acoustic maps) and visual observations of levitation of plastic spheres in different nodes. The experiments also showed that the most suitable acoustic pressure profiles are formed when the reflector with a curvature radius of 30 cm was used.

Heating

The suspended sample is heated by a Synrad Evolution 125 CO₂ laser with a maximum output power of 125 W. A schematic diagram of the sample heating system is shown in Fig. 3. The output power of the laser beam is preset in the range of 1 – 100 % of its maximum. The laser is pulsed to increase the degree of control over sample heating. The pulse duration is controlled by a Chronetics PG-12 pulse generator gating the laser controller. The laser beam is completely enclosed within a beam-guiding system (Laser Mechanisms, Inc.) that includes two mirrors (beam benders) directing the beam as necessary, laser flange and chamber flange adapters, and extendable tubes enabling one to readily adjust the external configuration. The laser beam is focused with a ZnSe lens. The lens is positioned so that the focal point lies 47 mm ahead of the levitating sample. Thus, the portion of the sample facing the incident beam is heated by a slightly defocused beam while a portion of the beam bypasses the sample to be reflected by a convex gold-coated copper mirror (Laser Components, Inc.) mounted behind the sample on the chamber wall. The reflected beam is re-focused by the mirror 23 mm behind the sample to heat the sample from the side opposite to the incident beam, ensuring more uniform heating. The construction enables some adjustment of the focal point of the incident laser beam by adjustment of the lens. The mirror sits on a vertical driver mirror mount (Thorlab) to adjust the reflected beam to coincide with the incident beam. Focusing and positioning of the beam is performed using the visible radiation of a laser diode aligned to coincide with the CO₂ laser beam.

The time required for effective sample heating was estimated for spherical zirconium oxide samples assuming uniform temperature distribution in the sample, radiative heat exchange only, and constant thermophysical parameters. The estimate is based on the following equation:

$$c\rho V dT/dt = Q - \varepsilon\sigma S(T^4 - T_0^4) - hS(T - T_0), T_0 < T < T_m \quad (1)$$

where t is time, T the sample temperature, T_0 the temperature of the environment and the initial temperature of the sample (room temperature, 298 K). V is the volume of the spherical sample, σ the Stephan-Boltzmann constant, and S is the surface area of the sample. The heat transfer coefficient h is expressed through the Nusselt number Nu , the thermal conductivity of the atmosphere λ_g , and the sample diameter d :

$$h = Nu\lambda_g/d. \quad (2)$$

The Nusselt number is set equal to 2, corresponding to a spherical particle in an unmovable medium. The sample is considered to be a black body with emissivity $\varepsilon=1$. The time required to completely melt the sample, Δt_{melt} , was found from the heat balance:

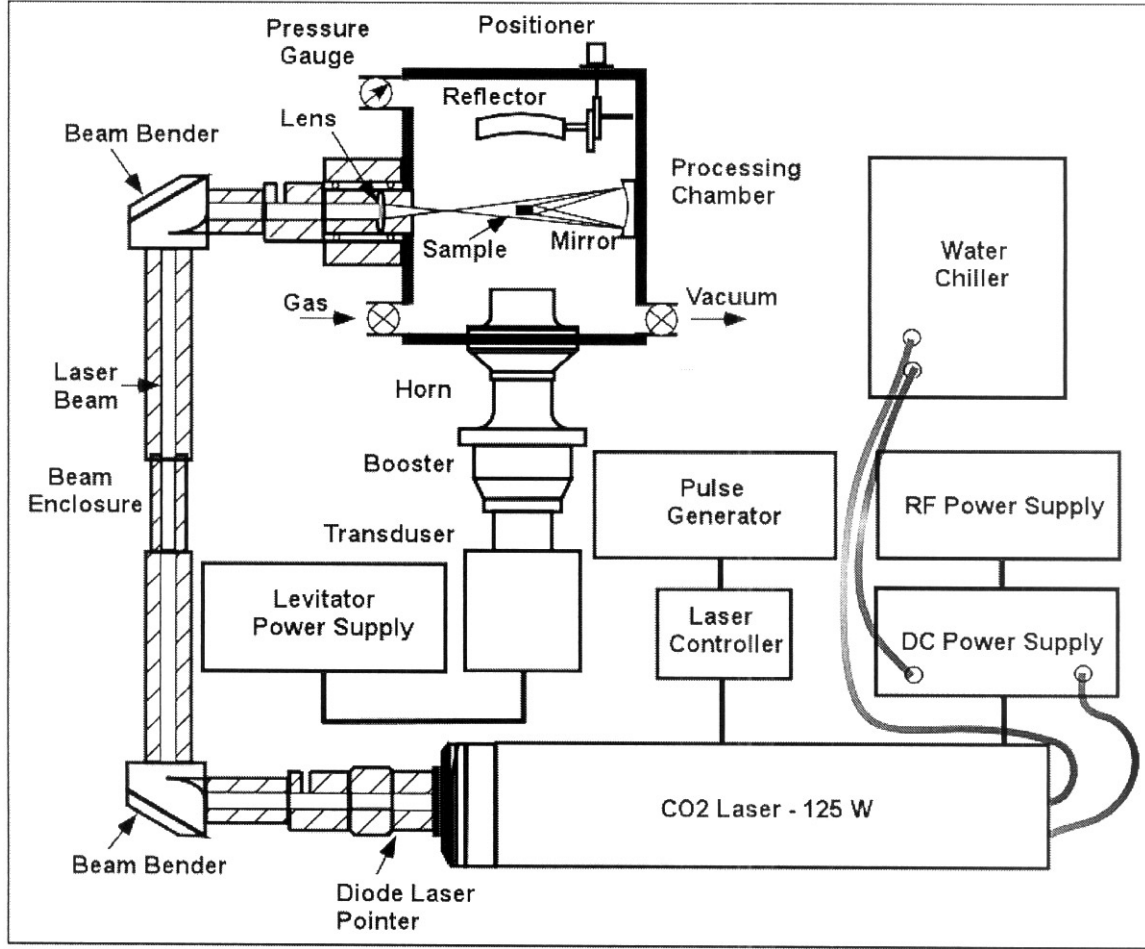


Fig. 3: Schematic diagram of the CO₂ laser and the sample heating system.

$$\Delta t_{melt} = \frac{\Delta H_{melt} \rho V}{Q - \epsilon \sigma S (T^4 - T_0^4) - h S (T - T_0)} \quad (3)$$

The parameters used in this estimate are shown in Table 1. Results for heating with 100 % power are shown in Fig. 4, plateaus in the heating curves indicate melting of the sample. According to these calculations, the largest sample that can be heated reliably is close to 3 mm in diameter. Larger samples could not be melted completely in the short time span available for experiments. Samples of 1 – 3 mm diameter provide enough material for subsequent analyses by SEM, TEM, and XRD, however.

Table 1. Parameters used to estimate the temperature of a spherical ZrO₂ sample vs. heating time. References are given where appropriate.

Melting temperature	$T_m = 2950 \text{ K}$	[18]
Enthalpy of melting	$\Delta H_{melt} = 706257 \text{ J/kg}$	[18]
Solid heat capacity	$c = 581 \text{ J/(kg}\cdot\text{K)}$	[18]
Melt heat capacity	$c = 713 \text{ J/(kg}\cdot\text{K)}$	[18]
Sample density	$\rho = 5600 \text{ kg/m}^3$	[19]
Thermal conductivity of argon	$\lambda_g = 0.06 \text{ W/(m}\cdot\text{K)}$	[20]
Heat source power	$Q = 125 \text{ W}$	
Emissivity	$\epsilon = 1$	

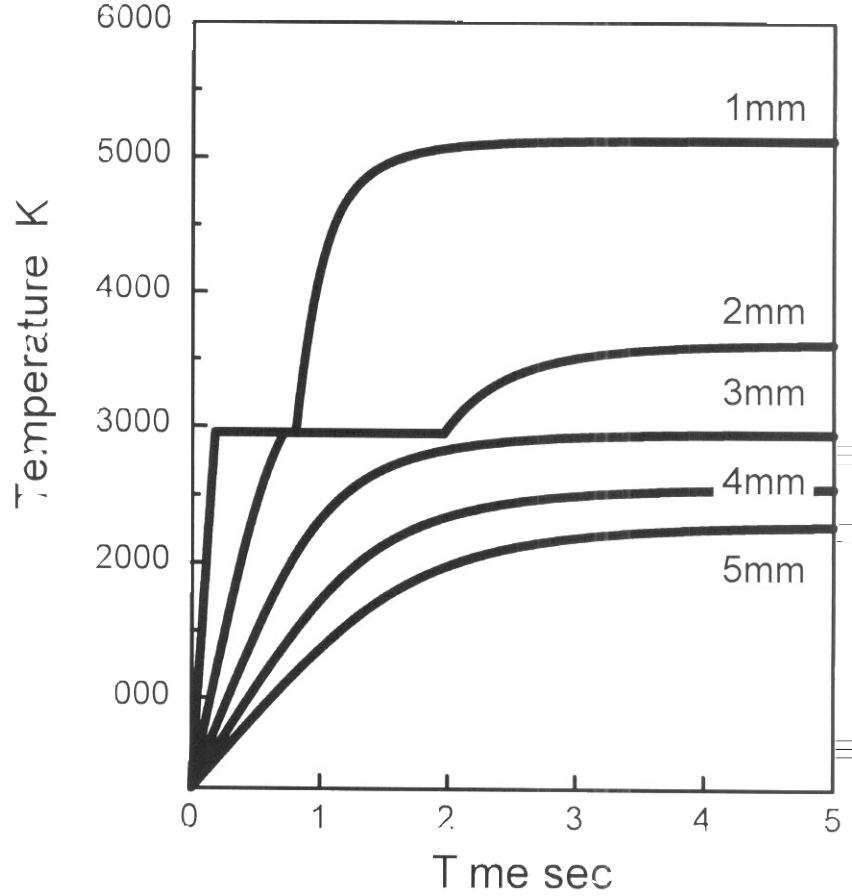


Fig. 4: Heating of spherical samples of various sizes.

The time the sample is kept at a high temperature should be sufficiently long to reach equilibrium. This time can be roughly estimated from diffusion rates and assuming that equilibrium is established after components diffuse over a distance equal to the sample diameter. Using the diffusivity coefficient of oxygen in zirconium, $D = 2.63 \cdot \exp(-118/RT) \text{ cm}^2/\text{s}$ (with R as the universal gas constant)[21], the estimated equilibration time t_{eq}

$$t_{eq} \approx \frac{d^2}{D} \quad (4)$$

is of the order of one second for a particle of 1 mm diameter at 2500 K. This diffusion coefficient is lower than that in the molten metal, this estimate can therefore be considered the upper limit for the equilibration time. Based on the above considerations, the total time required for heating and compositional equilibration of samples with 1 – 3 mm diameter is on the order of several seconds—less than the 20 - 25 s available during one parabolic trajectory.

Monitoring the experiment

Sample temperature and chamber pressure are monitored by a three-color optical pyrometer and a pressure gauge, respectively. Changes in sample appearance caused by any reaction are recorded visually by a video camera. Additional diagnostics, e.g. sampling the atmosphere post-experiment for subsequent compositional analysis, or monitoring the temperature of the atmosphere surrounding the sample, will be used if needed. A computer is used for data acquisition.

Currently, the experimental setup has been assembled and is being tested in normal gravity. In preliminary experiments, the laser pulse and the quencher are triggered manually, while an electronic controller will be developed for the microgravity experiments. A fully automated control and data acquisition system is being designed based on LabView (National Instruments). The experimental control and data acquisition system is shown schematically in Fig. 5. Gating of the laser pulse, the levitator power, motion of the wire screens and the quencher all will be controlled electronically. Controlled feedback between pyrometer and laser gating will enable one to adjust laser power and pulse duration to achieve and maintain target temperature. Interlock switches are mounted on the chamber doors to interrupt the laser power supply when the chamber is opened.

Quenching

The hot sample is rapidly quenched between two colliding brass blocks. The blocks are mounted on spring-loaded arms, which are triggered mechanically from outside the chamber via a push rod. The quenching mechanism is illustrated schematically in Fig. 1. During the quench, the sample is sandwiched between the brass blocks and solidifies as a thin platelet.

The quench rate achievable this way was estimated to be on the order of 10^6 K/s for Zr metal assuming that the thickness of the platelet is about 100 μm and the material is quenched from the melting point (2130 K) to room temperature. This rate is comparable to quench rates achievable by splat quenching [22].

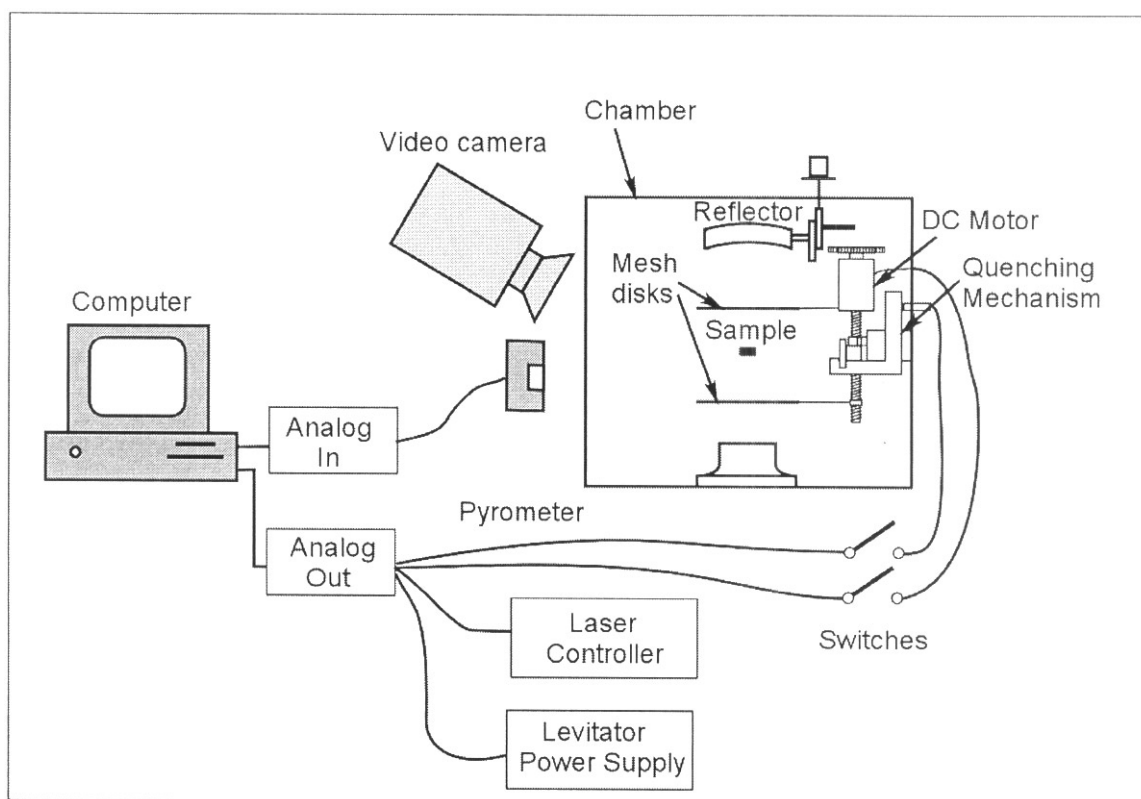


Fig. 5: The diagnostics/control of the experiment.

Preliminary results

Spherical samples of various materials and sizes have been successfully levitated. Sample masses ranged from 0.01 g to 0.12 g, the diameters from 3.14 mm to 4.3 mm. For each pressure node, the reflector

can be moved a limited distance from an optimum position while still effectively levitating the sample. Depending on sample mass and on which pressure node was used, the maximum possible displacement observed varied between 2.3 and 30 mm. The relation of reflector displacement vs. sample displacement is needed for rapid adjustment of the setup since the stable sample position for each node will be slightly higher in microgravity than it is in normal gravity. Some of the results of the experiments that gives this relation are presented in Table 2.

Experiments with simultaneous levitation and heating were carried out as well. While levitated samples could be stabilized in the focus of the laser beam, attempts to heat the sample to a stable target temperature in normal gravity were unsuccessful. As a result of sample heating, levitation becomes unstable, and the sample falls off. Consistent with earlier reports [23], heating of the sample was found to change the properties of the acoustic field, thereby destabilizing the levitating sample. Convection and acoustic streaming, arising from the interaction of the acoustic field with the obstacles (reflector, chamber walls and the sample) were previously shown to also affect levitation [24]. In the absence of convection under microgravity conditions, it is expected that the acoustic field is sufficient to stabilize samples long enough for effective laser heating.

Table 2. Possible reflector displacements without loss of levitation capability for various spherical samples.

MATERIAL OF LEVITATED SAMPLE	DIAMETER, MM	MASS, G	PRESSURE NODE DISTANCE FROM THE ACTUATOR, MM	REFLECTOR DISPLACEMENT, MM	SAMPLE DISPLACEMENT, MM
PLASTIC	3.14	0.01	41.5	30.0	17.7
			30.5	16.0	9.0
GLASS	4.30	0.12	41.0	5.0	3.6
			30.5	2.3	2.3
GLASS	3.70	0.08	41.5	3.4	-
			31.0	4.8	-
ALUMINUM	3.16	0.04	40.1	4.2	2.1
			30.5	4.4	1.8

Summary

An apparatus for containerless experiments under microgravity conditions onboard the KC-135 aircraft for the study of high-temperature phase equilibria in molten-metal based systems has been designed and built. The estimates show that mm-sized samples can be heated and equilibrated during one parabolic trajectory of the KC-135 aircraft. This size is also sufficient for subsequent phase analysis (SEM, TEM, XRD). Preliminary tests in normal gravity using samples suspended on a ceramic fiber are used to develop the electronic control and data acquisition system.

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THE EFFECT OF SIMULATED MICROGRAVITY ENVIRONMENT OF RWV BIOREACTORS ON SURFACE REACTIONS AND ADSORPTION OF SERUM PROTEINS ON BONE-BIOACTIVE MICROCARRIERS

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Abstract

Biomimetically modified bioactive materials with bone-like surface properties are attractive candidates for use as microcarriers for 3-D bone-like tissue engineering under simulated microgravity conditions of NASA-designed rotating wall vessel (RWV) bioreactors. The simulated microgravity environment is attainable under suitable parametric conditions of the RWV bioreactors. Ca-P containing bioactive glass (BG), whose stimulatory effect on bone cell function had been previously demonstrated, was used in the present study. BG surface modification via reactions in solution, resulting formation of bone-like minerals at the surface and adsorption of serum proteins is critical for obtaining the stimulatory effect. In this paper, we report on the major effects of simulated microgravity conditions of the RWV on the BG reactions surface reactions and protein adsorption in physiological solutions. Control tests at normal gravity were conducted at static and dynamic conditions. The study revealed that simulated microgravity remarkably enhanced reactions involved in the BG surface modification, including BG dissolution, formation of bone-like minerals at the surface and adsorption of serum proteins. Simultaneously, numerical models were developed to simulate the mass transport of chemical species to and from the BG surface under normal gravity and simulated microgravity conditions. The numerical results showed an excellent agreement with the experimental data at both testing conditions.^{1,2}

Introduction

Studies from space flights over the last two decades have demonstrated that there are basic physiological changes in humans during space flight, including severe loss of calcium and mineralized bone.³ Microgravity has been noted to modify the function of the bone cells and disturb metabolism.⁴ With the planned long duration space travel and stay, there is a great need to gain a fundamental understanding of the effect of microgravity on human bone cell function. Several aspects of microgravity conditions of outer space can be simulated on earth using NASA designed Rotating Wall Vessel (RWV) bioreactors.⁵ In the RWVs, cells may be seeded on suitable microcarriers and their function determined in comparison to the function under normal gravity conditions. An important aspect is the development of a “suitable” microcarrier to successfully enable the study of this problem in simulated microgravity. In this study we hypothesize that studies focusing on understanding bone loss are conducted in a near optimal way if the microcarriers have properties akin to those of the bone mineral phase.

Keywords: simulated microgravity, microcarriers, protein adsorption, surface reactions, 3D tissue engineering, biomaterials

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Ca-P containing bioactive glass (BG) as a material, which forms bone-like minerals upon immersion in physiological solutions, is a suitable microcarrier material for the fundamental studies of microgravity on bone cell function. As was demonstrated in our previous studies, surface modified BG produces a major effect on bone cells; namely, osteoprogenitor cells are upregulated to osteoblasts.⁶ This effect on cells is obtained by modifying the glass surface in solution.⁶ This treatment results in surface reactions and in the formation of a Ca-P layer at the BG surface. In solution, this surface can further transform to a bone-like mineral, i.e., carbonated crystalline hydroxyapatite (c-HA)⁷ We have also demonstrated that this transformation is dependent on the composition of the milieu in which the glass is immersed including the presence or not of proteins.^{8, 9} It further followed from our work that there is a selective adsorption of attachment molecules (fibronectin) without conformational changes that would affect their ligand function.^{6, 10} As a material with the unique, bone-like surface properties, this surface modified bioactive glass is an attractive candidate for use as microcarrier material for 3-D growth of bone-like tissue under simulated microgravity conditions of the RWV bioreactors. Considering that the RWV environment is completely different from conditions previously used for BG testing at normal gravity, determination of the BG surface reactions in the RWV was required.

In this paper, we report on the effect of simulated microgravity on the BG surface transformation reactions. We used the NASA designed High Aspect Ratio Vessel (HARV) for simulating the microgravity conditions. We describe the choice of experimental parameters, which ensured simulated microgravity conditions of BG particles in the HARV, the immersion experiments, and the analysis of BG reactions. We also describe the results of a numerical study of the transport of momentum and species in the HARV for the experimental conditions employed in this paper.

Materials and Methods

Bioactive glass 45S5⁷ (Mass %: 45.0 % SiO₂, 24.5 % CaO, 24.5 % Na₂O and 6.0 % P₂O₅) granules obtained from a commercial source (Mo-Sci Corp., Rolla, MO) were used for the study.

Method development

Numerical. The simulated microgravity environment of the RWV is completely different from conditions previously used for BG testing. These unique dynamic conditions are characterized by a lack of sedimentation of the particles immersed in the medium, viscous flow (low Reynolds number flow), low turbulence, low shear stresses at the particle interface, and a dual mass transport mechanism – diffusion and convection. Since the RWV is completely filled with an air bubble-free medium, the fluid motion is not affected by wall boundary layers.¹¹

It is known that a small microcarrier particle normally remains suspended in the RWV, as centrifugation and the fluid drag force balance sedimentation. For conditions used in this study, the resulting time-averaged microgravity experienced by the particle is evaluated to be ~ 0.01 g.

Simulated microgravity conditions for high-density (2.5 g/cm³) BG particles could be effectively maintained by using proper experimental parameters. The choice of the parametric conditions was based on the numerical simulation of the motion of a microcarrier particle in the RWV. In particular, the motion of a single spherical BG granule in the HARV was calculated using the methods described by Gao et al.¹¹ After considerable numerical experimentation, parameters for computation were set as follows: granule size range: 40-70 μm, rotating speed: 10 rpm, the liquid density and viscosity: $\rho_l = 1.0 \text{ g/cm}^3$ and $\mu = 0.01$

g/(cm · s). The trajectory of the particle was numerically evaluated in both an inertial and a rotational frame. The trajectories of a 40 µm or a 70 µm particle in the inertial frame of reference (Figure 1 a, b) display a very slow movement of the particle of either size away from the initial location. This suggests that the BG particles of this size range will move along with the bulk fluid for an extended duration of time.

Experimental

Simulated microgravity conditions. A High Aspect Ratio Vessel (HARV-50 ml, Synthecon, Houston, TX) which rotates about a horizontal axis was used to simulate the microgravity environment.

On the basis of the computational study, we selected a BG granule size 40 - 70 µm and a rotational speed of 10 rpm to maintain simulated microgravity conditions in the HARV. Considering that the choice of the experimental parameters was based on the numerical analysis of the motion of a single spherical BG particle, further experimental validation of simulated microgravity conditions for the actual testing conditions involving many particles of an irregular shape was required. This was conducted as follows.

A trial experiment to observe the trajectory of the granule movement in a HARV environment was performed using the chosen experimental parameters. The BG particles were loaded in the HARV at a 1mg/ml mass-to-solution-volume ratio. The calculated quantity and the total surface area of particles loaded at this ratio were 350×10^3 and 24 cm², respectively. The trial experiment was conducted using Au sputter coated BG granules. The Au surface film rendered the particles visible in solution. The observations confirmed that most of the particles, loaded in the HARV using the parameters selected, circled around the central region of the rotating chamber during the 24 hours of observation time. There was no evidence of clustering or aggregate formation during particle rotation in the HARV. Thus, the trial experiment confirmed that, for the selected experimental parameters, simulated microgravity conditions were in fact maintained in the HARV within the time frame of the experiment.

Control unit gravity conditions. BG behavior under simulated microgravity conditions of the HARV was compared with that at normal gravity. Control tests at normal gravity were conducted at both static and dynamic conditions. Well-controlled flow conditions were used for both control experiments. In comparison to the simulated microgravity conditions of the HARV, the static conditions provided a stagnant, surface shear and convection-free environment. Initially, we planned to conduct both control experiments in the HARV. However, a trial experiment showed that the BG behavior under static conditions of the HARV was similar to that in static vials. In view of this, the rest of control experiments at static conditions were conducted in static vials.

In order to determine the effect of gravity on the BG behavior in a parametric study, the control dynamic (motion) test at unit gravity was also conducted in a well-controlled environment of the HARV. The NASA-designed HARV normally rotates around a horizontal axis to create simulated microgravity conditions (HARV, micro-g). A modified HARV, which rotates around a vertical axis, was used for dynamic control studies at normal gravity (HARV, unit-g). In order to perform this experiment, a support system, needed to keep the HARV base in a vertical position, was designed and built. The rest of testing parameters, such as rotational speed (10 rpm), particle size, the ratios of particle mass and surface area to solution volume, were kept identical to before. Thus, the only difference between the two dynamic tests in the HARV was the presence or the absence of simulated microgravity.

Immersion experiments. All immersion experiments, either under simulated microgravity conditions or control unit gravity conditions, were conducted using previously developed test protocols.⁸

Immersion to study BG physico-chemical reactions. These immersion experiments were conducted using three types of simulated physiological solutions: ion- and serum-free tris buffered solution (solution denominated T, pH 7.4 at 37°C); this solution complemented with electrolytes typical for plasma (TE), and TE with 10% serum (TES). The BG particles were immersed at a 1 mg/ml mass-to-solution volume ratio. The corresponding surface area-to-solution volume ratio was 0.48 cm⁻¹. All solutions were pre-warmed to 37°C prior to immersion. The duration of immersion in T was 1, 3, 6, 10 and 24 hours. The immersion time was extended to 48 hours in TE and TES. At least two samples were used for each of the immersion periods.

Post-immersion, the solutions were analyzed for changes in the Si, Ca and P-concentrations using atomic absorption spectrophotometry (5100 PC, Perkin Elmer, Norwalk, CT) or colorimetry (UV-visible spectrophotometer, Ultraspec Plus, Pharmacia Biotech, Piscataway, NJ). The change in surface character of the BG particles was determined using diffuse reflectance Fourier transform infrared spectroscopy (FTIR) (5DXC, Nicolet, Madison, WI).

Immersion to study the adsorption of serum proteins. BG particles used for the protein adsorption study were either unmodified (BG-UN) or modified. When modified, either an amorphous calcium phosphate (BG-ACP) or a carbonated hydroxyapatite (BG-HA) was formed at the BG surface. For adsorption of serum proteins, BG particles were immersed in a typical tissue culture medium (Minimum Essential Medium, MEM) complemented with 10% newborn bovine serum for 2 hours. Proteins were extracted by treating BG particles with 1% Triton-X100 solution three times. The concentration of extracted proteins was measured using Bio-Rad detergent compatible (DC) assay and colorimetry at 750 nm. The amount of extracted proteins was normalized for particle weight.

Results and discussion

The effect of simulated microgravity on BG reactions in solution. Changes in the [Ca], [P] and [Si] as a function of BG immersion time and immersion conditions (simulated microgravity conditions of the HARV versus control conditions), are illustrated in Figure 2. The data show that the BG reactions in all solutions tested (T, TE, and TES) include leaching of all ions, followed by P-uptake and a slowing down of the Si- and Ca-release rate. Although the sequence of the reactions, typical for BG, was observed under both control and simulated microgravity conditions, the kinetics of the reactions and the reaction products were noticeably different.

Table 1. Rates of ion release under simulated microgravity (micro-g) conditions of the HARV versus control unit gravity (unit-g) conditions

Ion	Release rate, $\mu\text{g}/\text{mg h}^{-1}$					
	T		TE		TES	
	micro-g	unit-g	micro-g	unit-g	micro-g	unit-g
SI	50.0	20.0	50.0	25.0	50.0	10.0
CA	80.0	25.0	55.0	5.0	60.0	4.8
P	12.0	2.0	7.0	0.7	ND	ND

Note: Release rates were determined at the linear portion of the ion release plots
nd – not determined

Table 2. Reaction products: [Ca]x[P] ionic product and total amount of P uptake ($M \cdot 10^{-3}$) Simulated microgravity (micro-g) conditions versus control unit gravity (unit-g) conditions.

Solution	[Ca] x [P]		P-uptake	
	micro-g	unit-g	micro-g	unit-g
T	1.04	0.11	0.35	0.03
TE	4.57	2.6	0.87	0.52

Note: The [Ca] and [P] values in the [Ca]x[P] product were determined as [Ca]max and [P] max released prior to P-uptake; P-uptake was determined as a difference between [P]max and [P]min

We determined the effect of simulated microgravity on the following parameters of BG reactions in solutions tested: rates of Si-, Ca- and P-ion release; the amount of ion release; the [Ca]x[P] ionic product, and the total amount of subsequent P-uptake. This comparative analysis revealed a remarkable increase in the rates of ion release in all solutions tested in the HARV (Tab. 1). For instance, in the case of immersion in T, the rates of Si-, Ca-, and P-release in the HARV were 2.5, 3.2 and 6 times greater than those under control conditions. Accordingly, the amounts of Si-, Ca-, and P-release also increased. The ion release in T, expressed as mass % of the original Si-, Ca-, and P-content in BG, was 30%, 60%, and 46.6% in the HARV in comparison to 11.1, 18.3 and 12.9% under control conditions.

The enhancement of BG dissolution under simulated microgravity conditions affected the subsequent BG reactions, which include solution saturation with Si-, Ca- and P-ions followed by BG surface stabilization and formation and growth of Ca-P phases. As shown in Figure 2, in comparison to control conditions, the surface stabilization (indicated by slowing down in the Si- and Ca-release) occurred much faster under simulated microgravity. The enhanced dissolution also resulted in about a 10-fold increase in the [Ca] x [P] ionic product (Tab. 2). This increase was followed by faster and greater P-uptake, which is indicative of growth of Ca-P phases at the BG surface. The time to P-uptake was reduced (1 vs. 6 hours in the HARV and control conditions respectively). There was about a 10-fold increase in the total amount of P-uptake (Tab. 2).

Therefore, the chemical analysis suggests that simulated microgravity environment of the HARV enhanced the BG dissolution and subsequent formation of Ca-P phases at the BG surface.

The effect of simulated microgravity on BG surface modification. FTIR spectra of the BG particles before and after immersion in serum-free TE under simulated microgravity (HARV micro-g) and control conditions are shown in Figures 3. Both control unit gravity tests, static and dynamic (HARV unit-g), were used for these experiments. The spectra after immersion show the presence of broad P-O bands, which were absent before immersion. These bands are characteristic for amorphous calcium phosphate (ACP),. Both control conditions showed weak P-O bands. In contrast, simulated microgravity conditions showed unusually large intensities of the P-O bands. Similar effect of the simulated microgravity conditions was observed on immersion in serum-containing TES. The large increase in the intensities of the ACP bands suggests a significant increase in the amount of the Ca-P phase at the BG surface under simulated microgravity conditions.

Thus, both chemical and FTIR analyses suggest that the formation of bioactive Ca-P surface was enhanced under simulated microgravity conditions of the HARV.

The effect of simulated microgravity on adsorption of serum proteins. Figures 5 a and 5 b show the amount of adsorbed serum proteins. Figure 5 a demonstrates the effect of BG surface modification on protein adsorption in unit gravity; and Figure 5 b shows the effect of simulated microgravity. It was found that the amount of proteins adsorbed onto unmodified BG-UN particles in unit gravity was 10 times larger than that reported for porous BG discs.³ In comparison to BG-UN, the amount of proteins adsorbed on modified BG-ACP and BG-cAp particles increased more than two and three times, respectively. The effects of ACP and c-HA phases on protein adsorption are in agreement with previous reports.³ The adsorbed amount became significantly greater under simulated microgravity conditions: the amount adsorbed onto both unmodified and modified BG doubled (a 100% increase).

The study demonstrated the major effects of a large surface (the mean surface area of 40-70 μm particles is 0.48 cm^2/g), surface modification, and simulated microgravity conditions on the adsorption of serum proteins on the BG microcarriers.

Numerical study

Simultaneous to the experimental study, numerical models were developed to evaluate the mass transport of chemical species to and from the BG surface under static and HARV conditions.² It may be noted that under static control conditions, diffusion is the mass transfer mechanism, while under simulated microgravity conditions of the HARV, mass transfer involved both diffusion and convection. As shown in Figure 4, the numerical results for time-dependent changes in the ion concentrations showed an excellent agreement with the experimental data at both static and HARV conditions.

The numerical study suggests that the unique dynamic conditions - lack of sedimentation, very low shear stress (1.0 – 1.5 dyne/cm^2), and the dual mechanism of the mass transport involving diffusion and convection – are likely to be at the basis of the enhanced BG surface reactions under the simulated microgravity conditions of the NASA-designed rotating wall vessel bioreactors.

Conclusions

- This pioneering study revealed the major effect of the unique dynamic simulated microgravity conditions of NASA RWV bioreactors on the surface reactions of bioactive glass (BG) microcarriers.
- These simulated microgravity conditions remarkably enhanced BG reactions in solutions; this enhancement was followed by the enhanced formation of bone-like minerals at the BG surface.
- The study also revealed a remarkable effect of a large surface area, surface modification and simulated microgravity on the adsorption of serum proteins on the BG surface.
- The study demonstrated that the surface reactions critical for BG to function as a substrate for 3-D bone tissue engineering are enhanced in the RWV bioreactors simulating microgravity conditions.
- These findings suggest that the unique, well-controlled, dynamic environment of the RWV bioreactors could be successfully used for engineering biomimetic properties of biomaterials.

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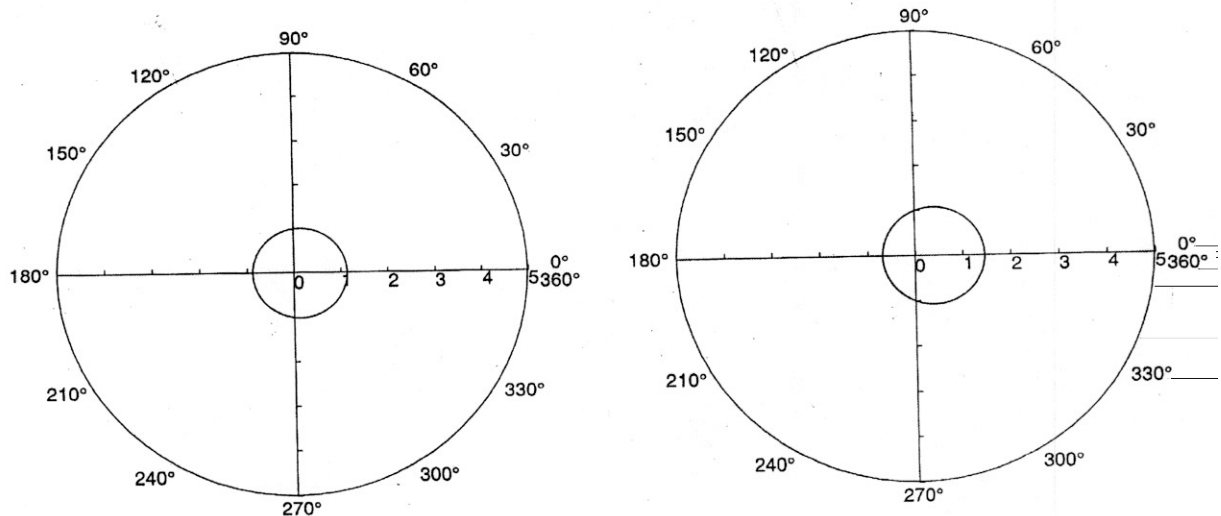


Figure 1. Trajectory of a round solid particle in the HARV in the inertial frame of reference at the selected experimental parameters: (a) $r = 20 \mu\text{m}$, (b) $r = 35 \mu\text{m}$; $\rho_p = 2.5 \text{ g/cm}^3$, $\omega = 10 \text{ rpm}$.

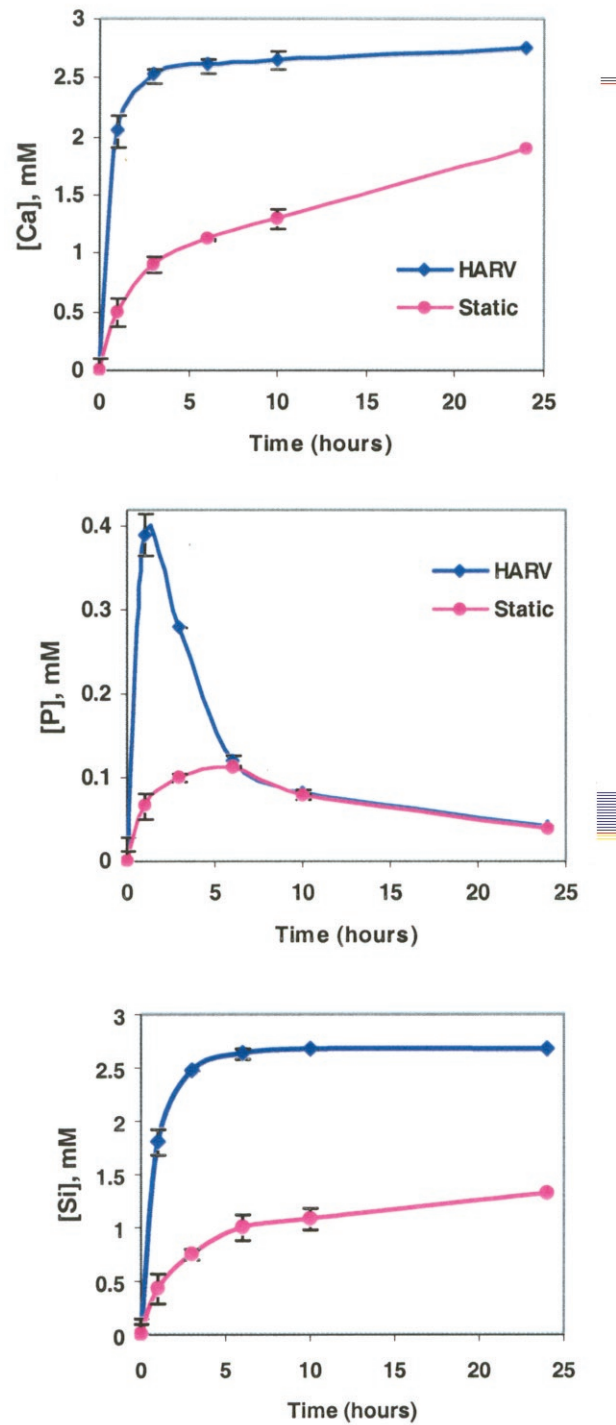
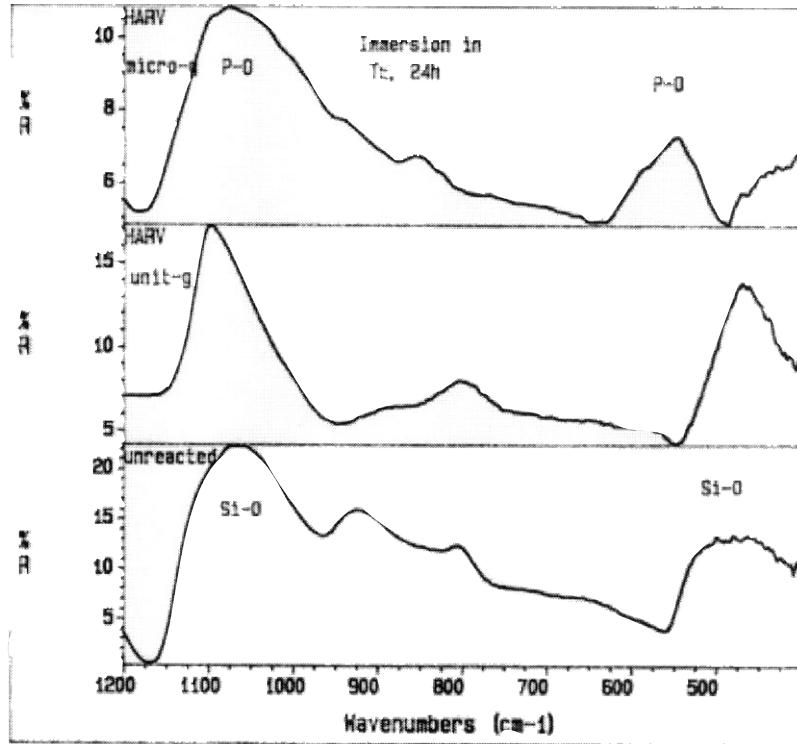


Figure 2. Changes in the [Ca], [P], and [Si] as a function of immersion time in ion- and serum-free T under simulated microgravity conditions of the HARV and control unit gravity conditions.



Figures 3 a, b. FTIR spectra of BG before and after immersion in serum-free TE under simulated microgravity (micro-g) and control unit gravity (unit-g) conditions. FTIR spectra of BG after immersion under both control conditions, static and dynamic, were similar.

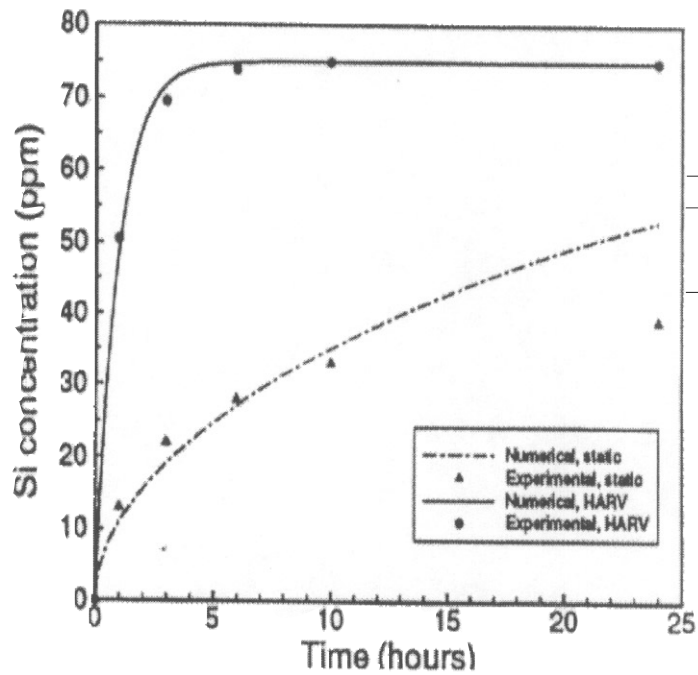


Figure 4. Numerical and experimental data for time-dependent Si-release in T under simulated microgravity conditions of the HARV and control (static) conditions.

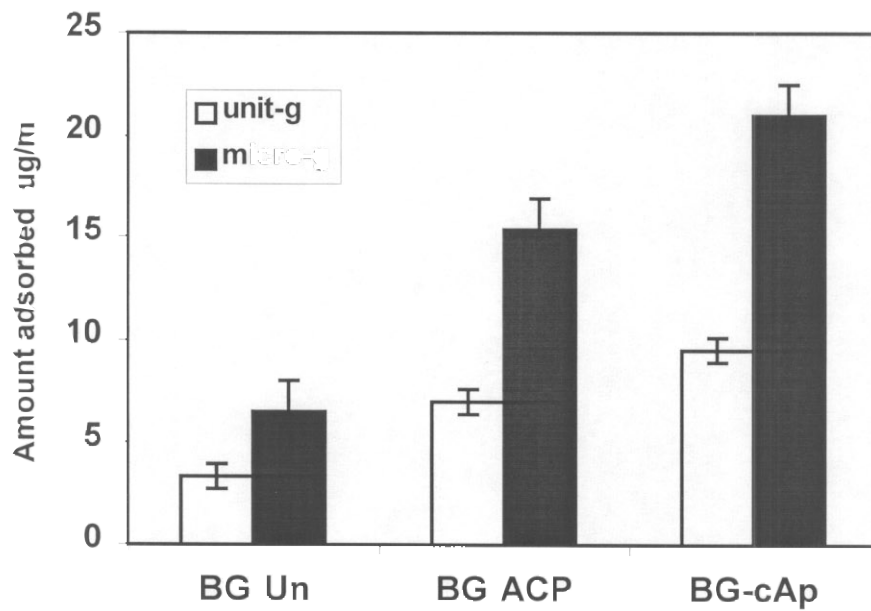
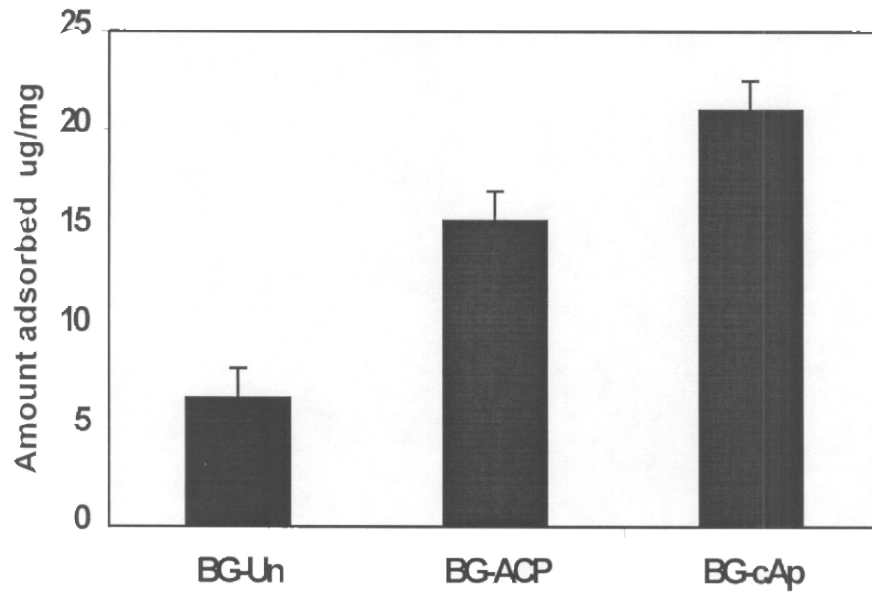


Figure 5 a, b. The amount of adsorbed serum proteins: (a) the effect of BG surface modification (unmodified BG-UN, modified to form amorphous calcium phosphate (BG-ACP), and modified to form carbonate apatite (BG-cAp)); (b) the effect of surface modification and simulated microgravity.

FUNDAMENTAL STUDIES OF CRYSTAL GROWTH OF MICROPOROUS MATERIALS

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Introduction

Microporous materials are framework structures with well-defined porosity, often of molecular dimensions. Zeolites contain aluminum and silicon atoms in their framework and are the most extensively studied amongst all microporous materials. Framework structures with P, Ga, Fe, Co, Zn, B, Ti and a host of other elements have also been made. Typical synthesis of microporous materials involve mixing the framework elements (or compounds, thereof) in a basic solution, followed by aging in some cases and then heating at elevated temperatures. This process is termed hydrothermal synthesis, and involves complex chemical and physical changes. Because of a limited understanding of this process, most synthesis advancements happen by a trial and error approach. There is considerable interest in understanding the synthesis process at a molecular level with the expectation that eventually new framework structures will be built by design. The basic issues in the microporous materials crystallization process include:

- Nature of the molecular units responsible for the crystal nuclei formation
- Nature of the nuclei and nucleation process
- Growth process of the nuclei into crystal
- Morphological control and size of the resulting crystal
- Surface structure of the resulting crystals
- Transformation of frameworks into other frameworks or condensed structures

The NASA-funded research described in this report focuses to varying degrees on all of the above issues and has been described in several publications.¹⁻⁹ Following is the presentation of the highlights of our current research program. The report is divided into five sections:

1. Fundamental aspects of the crystal growth process
2. Morphological and surface properties of crystals
3. Crystal dissolution and transformations
4. Modeling of crystal growth
5. Relevant microgravity experiments

1. Fundamental aspects of the crystal growth process

1.1 Reverse micellar system and microporous zincophosphate synthesis

We have focused on a novel synthesis medium to provide basic information about microporous crystal growth. Reverse micelles are thermodynamically stable systems, where ionic and nonionic surfactant

Keywords: zeolite, reverse micelle, modeling, nanoparticles, AFM

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molecules in hydrocarbon solvents solubilize water in small nanoclusters. The water pool of the reverse micelles have been used extensively for synthesis of a wide range of size-quantized dispersed inorganic nanoparticles.¹⁰ We were the first to report that microporous materials can also be synthesized under the appropriate conditions in reverse micellar reactants.^{7,8} Figure 1 compares the frameworks of sodalite, faujasite, zeolite A and hopeite which are relevant to the present study.

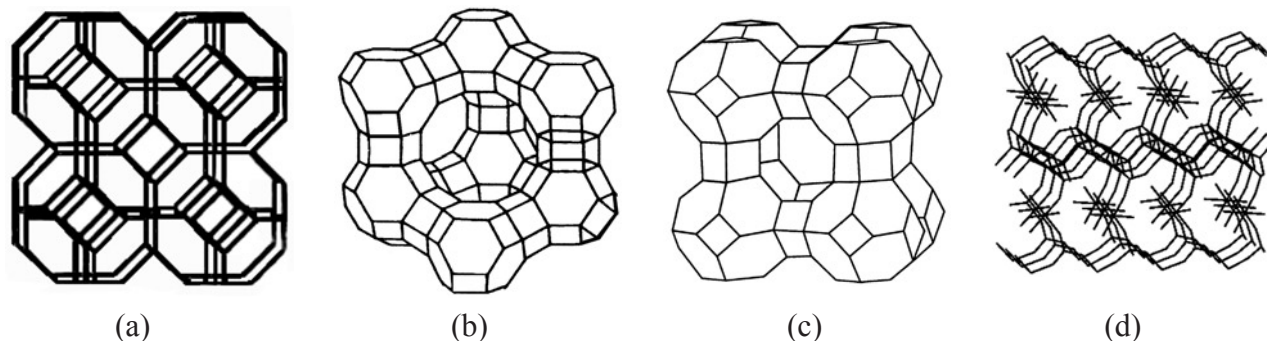


Figure 1. Framework structures of (a) Sodalite, (b) Faujasite, (c) Zeolite-A and (d) Hopeite.

The reverse micelle based synthesis of microporous materials involves mixing together reactants contained in reverse micelle solutions. The important steps in formation of crystal nuclei involve exchange processes between reverse micelles, as depicted in Figure 2. Because the reactants remain encapsulated in reverse micelles throughout the synthesis process, the chemistry within the nanometer sized water pools determine the crystal growth dynamics.



Figure 2. Exchange processes in reverse micelles.

1.1.a Sodalite system. The most extensively used surfactant for reverse micelle synthesis is sodium bis(2-ethylhexyl) sulfosuccinate (AOT). We have reported the synthesis of zincophosphate sodalite (ZnPO-S) microporous material using AOT reverse micelles.^{7,8} If reactant composition is chosen such that only a small fraction of the micelles have the right supersaturation to form nuclei, then these nuclei can commence crystal growth using up the non-nucleated reverse micelles. After the crystals reach a certain size, they begin to settle via gravity, avoiding further growth in size. On the other hand, if the reactant composition is such that supersaturation is exceeded in a large fraction of the micelles, then rapid precipitation of an amorphous solid can occur, resembling the conventional synthesis. This control over crystallization pathways by minor changes in the reactant composition is unique to the reverse micellar medium and is a reflection of chemistry within the water pools.

However, AOT-based reverse micelles could not be used for synthesis of open frameworks. The aqueous environment within the AOT reverse micelles was not appropriate for microporous material synthesis.⁶ Use of cationic reverse micelles, especially the two-tailed surfactant dimethyldioctylammonium chloride (DODMAC) resulted in the successful synthesis of faujasitic ZnPO-X.^{4,5}

1.1.b Faujasitic System (ZnPO-X). The primary goal of using DODMAC reverse micelles was to synthesize porous zincophosphate frameworks, in particular ZnPO-X. Two templating agents have

been studied, tetramethylammonium ion (TMA^+) and 1,4-diazabicyclo[2,2,2]octane (DABCO). Mixing proper ratio of Zn, phosphate and TMAOH containing reverse micelle solutions (made by the equilibration method) produced ZnPO-X crystals. Upon ultracentrifugation of the mother liquor before any cloudiness was visually evident, a small amount of solid was recovered. These suspended crystals are small, on the order of a few hundred nm. Enough sample could not be recovered for diffraction analysis, but micro Raman spectroscopy showed bands at 765, 983, 1014 and 1119 cm^{-1} , characteristic of faujasitic zincophosphate (ZnPO-X).⁶

With DABCO as templating agent, the DODMAC reverse micelles were made by an injection method. Light scattering experiments showed that the diameter of the **Zn** and **P** containing reverse micelles were 8 nm and 6 nm respectively. Reaction was carried out by mixing the **Zn** and **P** micelles with volume ratio of 1:1. Powder diffraction patterns as well as the octahedral morphology confirm the formation of the ZnPO-X structure. The yields of zincophosphate X were of the order of 15-20%, indicating that a large fraction of the zinc and phosphate species were still present in the micellar medium, with the size of the clusters remaining in solution being of the order of 15 nm.⁴

1.2 Nucleation and Control of Crystal Growth

1.2.a Reverse Micelle System. Reverse micellar systems also provided a novel medium for studying “seeding” phenomena in growth of microporous materials. The addition of seed crystals to speed up the crystallization process has been practiced for microporous material synthesis for four decades.¹¹ The mechanism for rate enhancement is eventually related to the small size seeds. Macroscopic seeds promote nucleation by providing nuclei that exists on their surfaces (secondary process) and small seeds by virtue of their high surface area consume reactants and grow rapidly into crystals.

We examined the hypothesis that the 15 nm particles left behind from a ZnPO-X synthesis had a memory of the crystal and should act as an effective seed solution. To use the mother liquor as an effective seed solution, a second micellar composition (**B**) was prepared. This composition does not produce ZnPO-X. Upon adding the mother liquor to composition **B**, uniform ZnPO-X crystals were produced. The seeding experiments were repeated in columns of heights 0.71, 1.78 and 2.62 meters, and the crystal sizes increased with average sizes of 3, 6 and 15 μm crystals of ZnPO-X.⁴

1.2.b Aluminosilicate System. Since the nanometer-sized entities left behind were found to be effective in growing crystals in reverse micelle system (Section 1.2.a), we have extended this concept to aluminosilicate zeolites. In this system we synthesize nanometer-sized zeolite particles in clear solution synthesis following procedures developed by Schoeman and coworkers.^{12,13} The yield of nanometer-sized zeolite particles synthesized in clear solution system is very low. This is in parallel to our observation for ZnPO-X reverse micelle synthesis. We propose that this is because certain nutrients are exhausted from the synthesis system, thus stopping the further growth of the nuclei or nano-particles already in the system. Our hypothesis is that the species remaining behind in solution has ‘memory’ of the system and if provided with nutrients, will grow into crystals.

To establish our hypothesis in aluminosilicate clear solution system, we chose zeolites Y, A and sodalite system. The framework structures of these zeolite systems are shown in Figure 1. The nanometer-sized particles of zeolite-Y, A and Sodalite were synthesized using previously published procedures.^{12,13} After removing the crystallized nano particles of zeolite material, the remaining clear solution was used

as ‘nuclei’ for seeding experiments. A composition of $15.2\text{TMA}_2\text{O}:\text{xNa}_2\text{O}:1.6\text{Al}_2\text{O}_3:45\text{SiO}_2:805\text{H}_2\text{O}$ was chosen as a source of nutrient solution for these experiments. The amount of sodium content was controlled by adjusting the pH of silica sol reactant to 8 by means of ion exchange using a cation-exchange resin, Dowex HCR-S(H^+). This reaction mixture produces small amounts of sodalite after 3 days. We have found that zeolites Y, A and Sodalite can be synthesized by using their respective ‘nuclei’ solution as seed (nutrient to seed volume ratio 8). Thus, synthesis of these zeolites namely Y, A and Sodalite from identical nutrient solutions demonstrates the memory effect of ‘nuclei’ seeds as the controlling feature in the crystallization. Previous studies have focused on macroscopic seeds. Our contribution has been to show that ‘memory’ of crystals is retained even in nanometer-sized particles that do not have characteristics of a well-formed crystal.

2. Morphological and Surface Properties of Crystals

2.1 Morphological Control

Morphological control of microporous crystalline materials via synthetic routes is important for several reasons. For instance, it provides information about parameters that control nucleation and crystal growth, thereby illuminating aspects of the synthesis mechanism. Also, control of morphology is important for targeting various applications. We have shown that by altering composition, the morphology ZnPO-X could be changed.⁹ Previously reported synthesis of ZnPO-X at 4°C led to the formation of crystals with the characteristic octahedral morphology of faujasitic structures. Sizes of these crystals are in the $<10\text{ }\mu\text{m}$ range. We found that by increasing the TMAOH/ H_3PO_4 and $\text{Zn}^{2+}/\text{Na}^+$ ratios, the morphology was drastically altered to produce large hexagonal platelet type crystals with diameters around $100\text{ }\mu\text{m}$. Figure 3 demonstrates the morphological change. Based on electron microscopy data, we concluded that the presence of twin planes was leading to crystals with the platelet-like morphology.

2.2 Surface Structure

We have observed significant differences between surfaces of the microporous crystals synthesized via conventional hydrothermal method and reverse micelle method. Such differences have implications in both the growth mechanism and the usefulness of the crystals for various applications. From the SEM images of ZnPO-X synthesized by hydrothermal (HS) and reverse micelle (RM) methods, surface smoothness was evident on the crystals made by the RM method. This is more evident in the AFM images of the crystals shown in Figure 4.

Previous studies have concluded, in general that zeolitic open frameworks both grow and dissolve by a layer-by-layer mechanism.¹⁴ Thus, at any time during crystal growth, a growing crystal face is bombarded by nuclei that can attach to the crystal face and start growing. Because of the random nature of the collisions, there are multiple nucleation sites on the crystal surface at which growth occurs. Eventually the growing faces meet and complete a layer on a surface, though during this time, crystal growth could have begun on top of the layer. Such a growth pattern will lead to multiple layers and we could readily distinguish ~ 20 -25 layers on the ZnPO-X crystal surface (Figure 4a). For aluminosilicate faujasites, a structure with similar framework as ZnPO-X, Anderson and coworkers¹⁴ noted triangular terraces with step heights of approximately $15\text{ }\text{\AA}$, which is the dimension of a faujasite sheet, and the present studies are consistent with these observations. Thus, it appears that the ZnPO-X HS sample has features very similar to those reported for aluminosilicate zeolites, and suggest similar growth mechanisms.

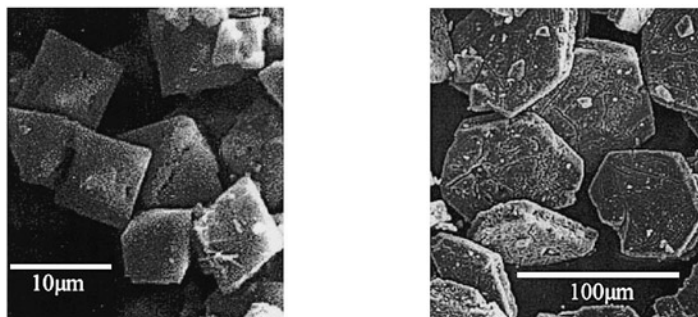


Figure 3. SEM micrographs of ZnPO-X crystals demonstrating the change in morphology from octahedral crystals (left) to platelet crystals (right).

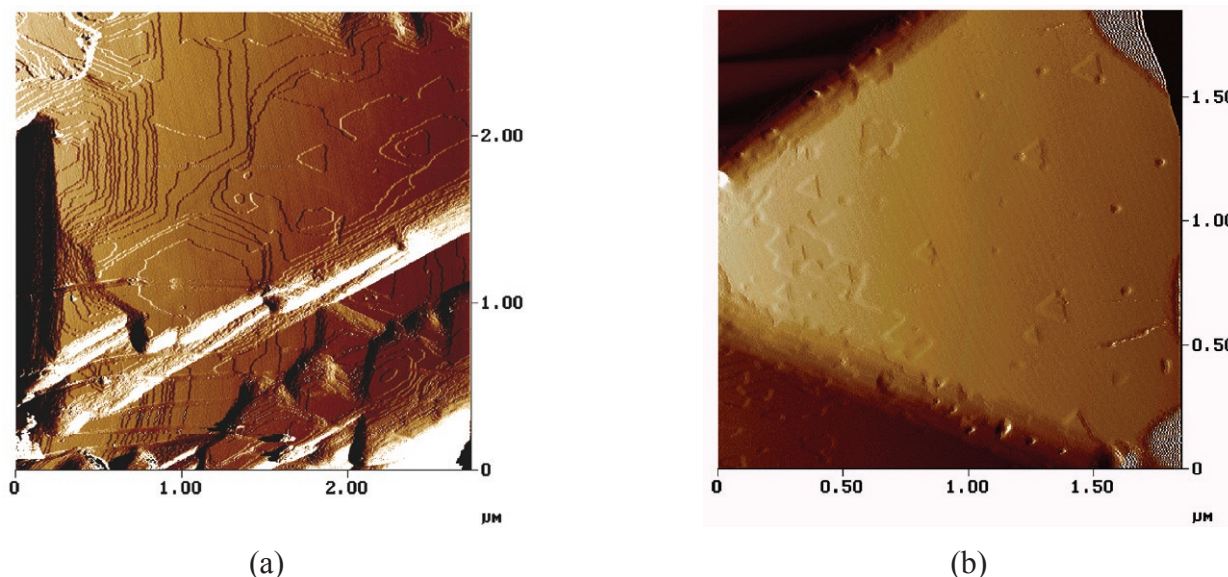


Figure 4. AFM images of the ZnPO-X surface synthesized via (a) hydrothermal synthesis method and (b) reverse micelle system.

On the other hand, crystals grown by the RM method show distinct differences from the HS grown crystals. Besides the differences in the surface roughness due to the lack of terraces on the (111) face, there is another important difference as is clear from Figure 4. The few triangular terraces noticed on the RM crystals have their orientations in registry with the overall crystals, with the apex of the triangle pointing to the crystal edges and not rotated, as was noted earlier for the HS grown crystals.

Nucleation in the RM system begins in tiny water droplets that are dispersed in an organic medium. Crystal growth proceeds by acquiring nutrients from the aqueous interior of the reverse micelles that collide with the crystal surface. Since the zincophosphate crystal is growing in an organic medium and the crystal surface is polar, it is likely that the growing crystal is covered by a film of water separated from the hydrocarbon by a layer of surfactant molecules. Such an arrangement will stabilize the polar crystal surface-hydrocarbon interface. Thus, when reverse micelles containing the nutrients collide with the crystal surface, its contents get distributed in the water layer surrounding the crystal. This water layer provides a means for the nutrients to re-equilibrate and provide building blocks for the growth of the crystal. The absence of terraces in the RM samples indicates that terrace nucleation is slower as compared to propagation of the layer across the surface.

The growth in the RM system is fundamentally different because of the presence of the protective surface water layer, which equilibrates and minimizes the number of species involved in crystal growth.

3. Crystal Dissolution and transformations

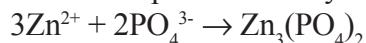
3.1 Dissolution of ZnPO-X

The possibility of synthesizing reasonably large flat crystals of ZnPO-X has made it feasible to do detailed Raman microprobe spectroscopic experiments. In particular, we have focused on microprobe Raman spectroscopy and examined how dissolution of ZnPO-X crystals occurs as a function of different monovalent cations in the medium.² The vibrational information obtained from Raman spectroscopy made it possible to analyze the structural changes at the molecular level. In the presence of H⁺, at a pH of 3, the vibrational bands due to ZnPO-X disappeared completely in 12 minutes. These were replaced by Raman bands of hopeite, Zn₃(PO₄)₂, a condensed form of zincophosphate. Electron microscopic experiments showed that the ZnPO-X was gradually getting covered with a film of hopeite. If, instead of H⁺, Li⁺, or Cs⁺ were used, then the ZnPO-X gradually converted to framework structures of LiA(BW) and CsZnPO₄, respectively. How H⁺, Li⁺ and Cs⁺ destabilize in the ZnPO-X structure was also manifested in the vibrational band of tetramethylammonium (TMA) ions trapped in the sodalite cages of ZnPO-X. Upon exchange with H⁺, Li⁺, and Cs⁺, prior to collapse of the ZnPO-X and loss of TMA from the Raman spectra, there is a significant broadening of the TMA band at 765 cm⁻¹. The bandwidth changes from ~ 6 cm⁻¹ for Na⁺ to 11,12 and 16 cm⁻¹ for H⁺, Cs⁺ and Li⁺, respectively. Our interpretation is that, upon ion-exchange with these cations, there is a distortion of the ZnPO-X framework, which makes the framework more susceptible to hydrolysis.

3.2 Influence of Framework Topology on Dissolution

Dissolution of ZnPO-X and sodalite crystals were carried out using a citrate buffer of pH 3, and methodology for measuring the differences in the dissolution dynamics were developed.¹ The powder diffraction data clearly indicates that in both ZnPO-X and ZnPO-S dissolution, hopeite [Zn₃(PO₄)₂] is being formed as the product at pH~3. Electron microscopy (Figure 5) shows that the morphology of the hopeite formed in both cases is quite distinct. In the ZnPO-X, the hopeite crystals are considerably smaller and form a dense coating on the surface of the ZnPO-X pellet. For ZnPO-S, the hopeite crystals are considerably larger, and do not completely cover the pellet surface.

Elemental analysis of the solution shows the presence of both zinc and phosphorus indicating the presence of M⁺(aq), Zn²⁺(aq) and PO₄³⁻(aq). Formation of hopeite occurs by the following reaction:



As the zincophosphate dissolves, supersaturation that initiates the nucleation of hopeite occurs around the pellet surface. The formation of hopeite is promoted because of its low solubility, K_{sp} being reported on the order of 10⁻³⁵.

A colorimetric method that monitors the pH change around the dissolving crystals provides a direct estimate of hopeite formation. Figure 6a shows a typical spectral change during dissolution. We have examined the dissolution of hopeite and find no change in pH around the dissolving crystal. The dissolution of the framework zincophosphate structures with Zn/P = 1:1, to form hopeite leads to the imbalance of Zn and phosphate that leads to the pH change. The increase in pH around the dissolving crystal can be readily explained as arising from reaction of PO₄³⁻ with H⁺ to form HPO₄²⁻/H₂PO₄⁻. Thus, any changes in pH that we observe during ZnPO dissolution can be related to the excess phosphate resulting from formation of hopeite. The larger change in pH for the ZnPO-X system (Figure 6b) is consistent with the elemental

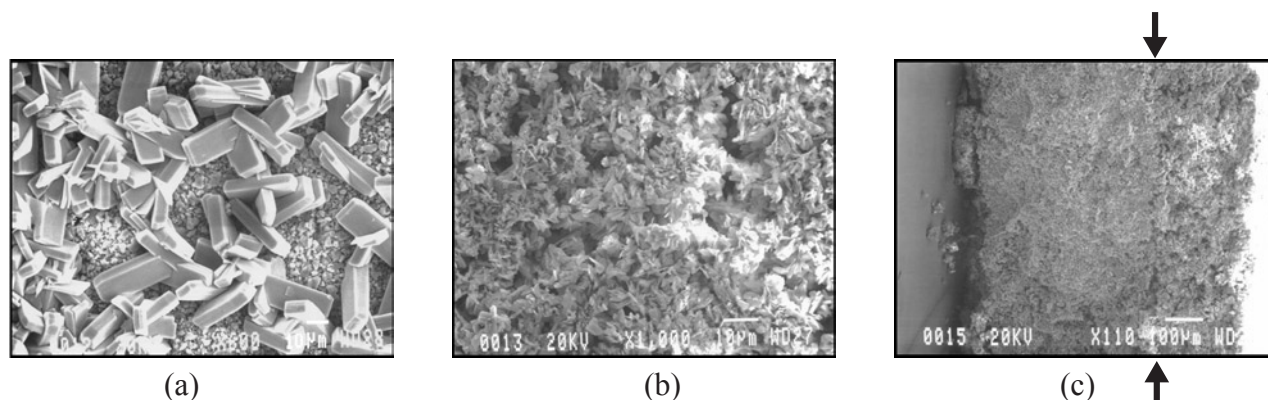


Figure 5. SEM micrographs of pellets of (a) ZnPO-S and (b) ZnPO-X after 1 hour of exposure to pH ~ 3 buffer (c) a side view of ZnPO-X after 2 hours of exposure to pH ~ 3 buffer (unstirred system). The layer to the right of the arrows is hopeite.

analysis data and supports the model that hopeite growth is more pronounced on ZnPO-X as compared to the ZnPO-S system.

3.3 Dissolution Mechanism.

The simplest possibility for hopeite formation is that the frameworks are dissolving to form Zn and phosphate, which then exceed supersaturation to form hopeite. However, considering the differences in morphology and the dynamics of hopeite formation and that the overall levels of solubilized zinc and phosphate are comparable, as seen from the elemental analysis, we do not favor this mechanism.

A more likely possibility is that the hopeite is nucleated on the surface of the dissolving crystal from the dissolution products prior to the species escaping into the solution. We propose the hypothesis that the nuclei of hopeite arise from intermediate dissolution products of the zincophosphate frameworks. Because of the differences in the framework structure and the access of protons to the framework, the dissolution units are structurally different, and result in formation of hopeite of distinct morphologies. Small crystals are expected to grow faster than larger crystals for diffusion-controlled processes. The pH studies indicate that the hopeite formation on ZnPO-X is more pronounced than ZnPO-S and could be a reflection of the smaller crystals and diffusion-controlled growth.

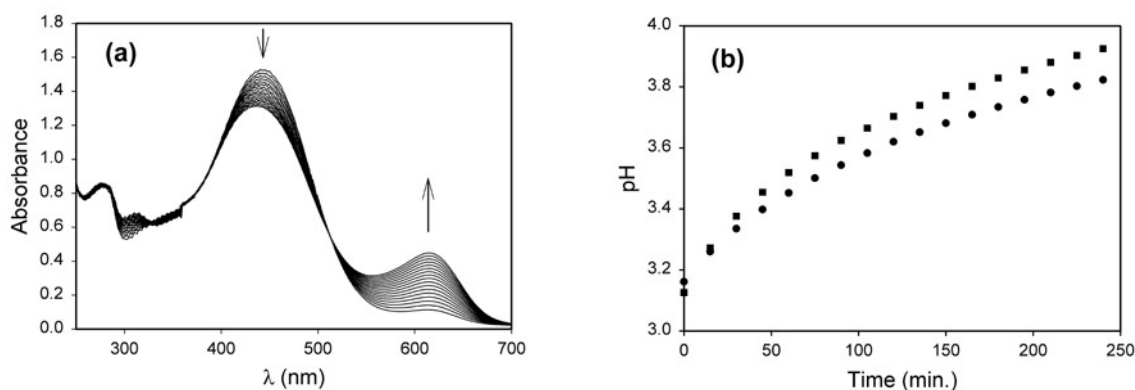


Figure 6. (a) Absorption spectra of the solution above a dissolving ZnPO-S pellet and (b) pH changes around dissolving ZnPO-S ($\bullet$) and ZnPO-X ($\blacksquare$) as a function of time (data taken every 15 min) in a solution containing bromocresol green buffered at pH ~ 3 (unstirred system).

4. Modeling of Nucleation and Crystal Growth

Thompson and coworkers have pioneered the Population Balance model to model zeolite synthesis.^{15,16} Recently there are reports of using population balance approach to study nucleation and crystal growth of nanoparticles such as CdS and CaCO₃ in reverse micellar systems.^{17,18} We are currently examining the feasibility of applying Population Balance modeling scheme to understand the nucleation and crystal growth of zincophosphate microporous materials from both reverse micelle based and hydrothermal synthesis.

4.1 Theoretical Development

The analysis that follows will be strictly limited to batch systems, that are, closed systems for which there is no exchange of mass with the surroundings.

If the particle size distribution of the population at any time during the process is given by $n = n(L, t)$, then the population balance for the batch system described above is

$$\partial n / \partial t + Q \partial n / \partial L = 0 \quad (1)$$

where t is time, L is some characteristic particle size, and Q is the linear growth rate. An initial condition and a boundary condition are necessary to uniquely specify the solution of the population balance equation. These are, respectively,

$$n(L, 0) = n_0 \quad (2)$$

$$n(r, t) = n_0 \quad (3)$$

where boundary condition at $L = r$ accounts for the size of particles at time t . Rather than solve the partial differential equation, Equation (1), it is more convenient here to make use of the moment transformation to generate a set of ordinary differential equations that can be solved more easily. Thus, if in Equation (1) each term is multiplied by L^i and then integrated over all possible particle sizes, the resulting set of moment equations is

$$dm_0/dt = 0 \quad (4)$$

$$dm_1/dt = Qm_0 \quad (5)$$

$$dm_2/dt = 2Qm_1 \quad (6)$$

$$dm_3/dt = 3Qm_2 \quad (7)$$

where the moments of the particle size distribution, the m_i 's, represent the cumulative number, length, area, and volume of particles, respectively. These can be solved far more easily than Equation (1), as long as the growth rate, Q , is known.

The size-independent growth rate is given by

$$Q(C) = k_g (C - C_{critical}) \quad (8)$$

where C is the concentration of the intermediate species, and $C_{critical}$ is the critical concentration of these species. It is assumed that the "activation reaction" sequence is solution occurs as



and that the transition from I (inactive) to C (active) occurs by some rate-limiting first-order reaction. As before, this assumption can be changed to reflect the specific nature of the chemical system of interest. The first-order reaction representation for the hydrolysis reaction has been used previously,¹⁹ and provides a relatively simple way of assessing the effect of a chemical conversion prior to the onset of the precipitation. To complete the formulation of the problem, then, materials balances for the inactive and the active species are written as

$$dI/dt = -k_p I \quad (10)$$

$$dC/dt = k_p I - \rho \phi Q m_3 / 2. \quad (11)$$

where ρ is the solid molar density (moles/cm³) and ϕ is the particle area shape factor (dimensionless). The last term in Equation (11) accounts for the consumption of active solution species by growth on existing particle surface.

Now to complete the formulation of the problem we must define the initial values. It is assumed that there is no nucleation and only the seed nuclei are growing, therefore, number of seed nuclei and hence the number of particles are constant throughout the reaction and it is known from the experimental data. Let the number of nuclei be n_0 . With further assumption that the seed particles are spherical and uniform in size the initial value of moments are calculated as follows:

$$m_0 = n_0 \quad (12)$$

$$m_1 = n_0 * (2r) \quad (13)$$

$$m_2 = n_0 * (4\pi r^2) \quad (14)$$

$$m_3 = n_0 * ((4/3) * \pi r^3) \quad (15)$$

where r is the radius of the initial ‘nuclei’ or ‘seed’ which can be determined experimentally. Now the initial values of all the moments are known because n_0 and r are known. Initially C is zero and $I = I_0$. Now the problem is well defined. The Equations (4)-(15) (excluding Equation 9 of course) will yield information regarding the growth of the seed nuclei in presence of a solution of limited inactive nutrients after an activation reaction in the solution phase.

4.2 Modeling of ZnPO-X seeded growth in reverse micelle system.

The equations noted above were solved using a standard fourth order Runge-Kutta integration procedure. For the preliminary results we are presenting here we made several assumptions to put the simulations in some perspective. We assume the reverse micelle nutrient solutions as a normal homogeneous clear solution. We also assume that Zn²⁺, PO₄³⁻ and DABCO ions act as a source of inactive species and there is formation of certain other ‘active’ species by combining these ions and that are contributing to crystal growth. The values of constants and parameters used in the simulation are given in Table 1. The change in concentration of both inactive, I , and active, C , species are shown in Figure 7a. It is observed that the concentration of inactive species decreases exponentially as expected according to Equation 10. The concentration of active species, C , increases to some level above the final value of 0.04 mole/cm³ and then decreases to this level as growth consumes the intermediate.

Table 1. Values of constants and parameters used in simulations.

Symbol	Value
I_0	0.05 mole/cm ³
$C_{critical}$	0.04 mole/cm ³
k_g	5.4 $\mu\text{m cm}^3 / \text{min mole}$
ϕ	6.0
ρ	1.0×10^{-14} mole/ μm^3
k_1	0.18 min ⁻¹
n_0	1.0×10^{10}
r	7.5×10^{-3} μm

The average particle sizes determined by light scattering are plotted in Figure 7b along with the experimental data, which shows that the simulation of average crystal size reaches to a final value. There is a time lag before crystals begin to grow. This time lag stems from the fact that the concentration of intermediate, C, must build up to a certain level, $C_{critical}$, before it can start attaching to the crystals to begin crystal growth.

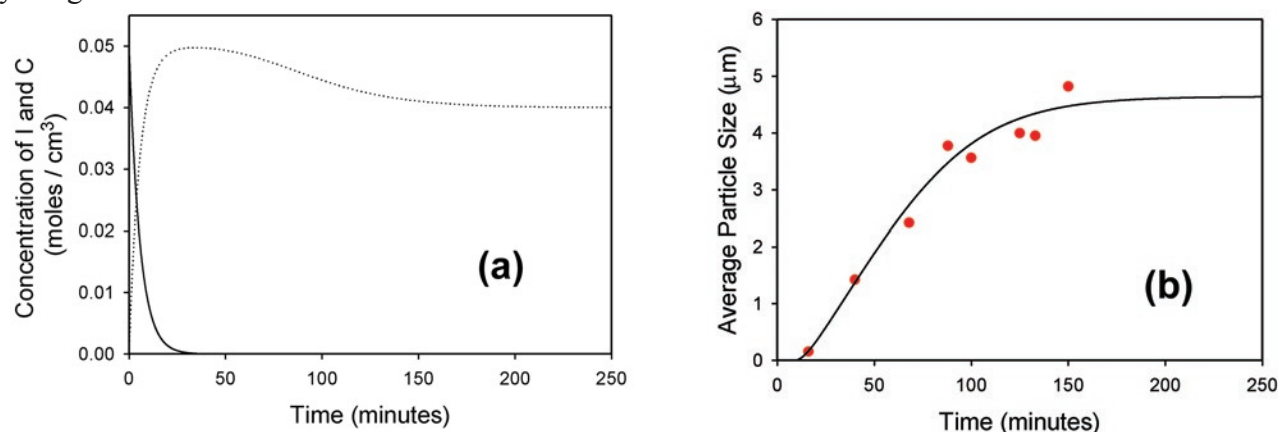


Figure 7. (a) Plot of variation of concentration of active and inactive species vs. time and (b) fitting of the calculated average particle size with the experimental data.

5. Proposed Experiments in Microgravity

Two major effects are manifested in microgravity. Under gravitational conditions, particles with densities greater than the fluid will settle with a terminal velocity as defined by Stokes law. Under microgravity conditions, the settling rate can be slowed down by 4 to 6 orders of magnitude. For example, in gravity of $10^{-4}g$, a 10-micron ZnPO particles will sediment about one cm in about 3 days. The second effect of microgravity is to reduce buoyancy driven convection. The convection process can be visualized as follows. The growth of the crystal leads to depletion of nutrients around it. This depleted volume will rise because it is lighter, leading to convection. This can limit the contact between the growing particle and nutrient as well as bring fresh nutrient towards the particle, thereby influencing crystal growth dynamics. Approximate calculations assuming a density differential of 0.01 g/cc lead to fluid flows of $10^{-4}cm/sec$ at $1g$, as compared to $10^{-6}cm/sec$ at $10^{-4}g$ around a 1 micron crystal of zincophosphate sodalite. Our goal is to exploit this effect to deduce information about crystal growth/dissolution.

5.1 Detachment Process

The goal here is to examine the difference in dissolution of two zincophosphate structures, sodalite and faujasite. There appears to be some consensus that growth of microporous structures occur by attachment of pseudocell units. *But, how do frameworks dissolve? Is it “atom-by-atom” or do polyhedral segments characteristic of the framework dissociates from the crystal.* If identical experiments are repeated on ground and microgravity, then from the measured velocity, the diffusion coefficient D_i can be unambiguously determined. Comparison of D_i between sodalite and faujasite structure fragments should readily indicate differences in size of the dissolving unit. Similar D_i 's will suggest dissolution by a pathway approaching an atom-by-atom dissolution.

5.2 Crystal Growth Experiments

The second set of experiments we propose to do in microgravity involves the growth of ZnPO-X and ZnPO-S from reactants in reverse micelles. Both these structures have sodalite units as building blocks, with the difference in microporosity arising from the packing of these units. We will examine the crystal growth dynamics for identical reactant compositions under microgravity and earth-based conditions using laser light scattering. *The hypothesis we want to verify is that the molecular complexity of the attaching species on a growing crystal surface changes with the framework.* At this stage, we are not proposing to discover the molecular structures of these species, but rather their complexity, e.g. are these atomic or polyhedral units? Typically, these pseudocell units have a convective-diffusive flow around the growing crystal. *Convection-driven shearing force will influence the rates of crystal growth differently for different frameworks.* The more complex the attaching species, the greater will be the influence of convection. The advantage of using the reverse micellar system is that a layer-by-layer crystal growth process is possible and the growth can be followed by light scattering. *Microgravity provides an environment in which the chemistry remains the same, yet the lack of convection can change the crystal growth dynamics for the same framework.* How this change is manifested differently for sodalite and faujasite is the information we are after.

Acknowledgement

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METALLIC AND INTERMETALLIC NANOPARTICLE FILAMENTS AND TREE-LIKE ASSEMBLIES PREPARED BY LASER VAPORIZATION CONTROLLED CONDENSATION

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Nanoparticles exhibit interesting properties that are usually different from the bulk materials' properties. The evolution of the nanoscale properties is largely dependent on the size, shape and assembly of the nanoparticles. The general objective of the ground-based experiments is to advance the scientific understanding of nucleation and materials synthesis from the vapor phase, which are strongly influenced by gravity and convection effects. In this work, we present a method to synthesize size-selected nanoparticles of a variety of materials by coupling the laser vaporization controlled condensation (LVCC) technique with a differential mobility analyzer (DMA). The LVCC method is based on using pulsed laser vaporization within well-defined conditions of temperature and pressure in a thermal diffusion cloud chamber. The coupling of LVCC and DMA is applied to synthesize Al, Fe, Ni, Ti and FeAl intermetallic nanoparticles of selected sizes.

The LVCC method can be coupled to plasma and ionic polymerization techniques, thus allowing the incorporation of the metallic nanoparticles within the polymer films. The size of the product polymer particles is limited in normal gravity by gravitational settling. The application of microgravity to the study of gas phase polymerization is expected to result in a better control of the process and may also lead to important technological advances. The effect of electrical charging of the nanoparticles by ions and free electrons generated by the laser vaporization process has been investigated. Enormous electrostatic aggregation due to dipole forces is observed between nanoparticles to form chain aggregates, and between the chain aggregates to form tree-like filaments. The tree-like aggregates may have special applications as fillers or additives to increase the elastic modulus and tensile strength of polymers such as low strength rubbers. These materials could have unique properties and may lead to new practical and technological applications.

Keywords: nanoparticles, intermetallic, polymer, filaments, tree-like

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MECHANISMS FOR THE CRYSTALLIZATION OF ZBLAN

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Abstract

The objective of this ground based study is to test the hypothesis that shear thinning (the non-Newtonian response of viscosity to shear rate) is a viable mechanism to explain the observation of enhanced glass formation in numerous low-g experiments. In 1-g, fluid motion results from buoyancy forces and surface tension driven convection. This fluid flow will introduce shear in undercooled liquids in 1-g. In low-g it is known that fluid flows are greatly reduced so that the shear rate in fluids can be extremely low. It is believed that some fluids may have weak structure in the absence of flow. Very small shear rates could cause this structure to collapse in response to shear resulting in a lowering of the viscosity of the fluid. The hypothesis of this research is that:

Shear thinning in undercooled liquids decreases the viscosity, increasing the rate of nucleation and crystallization of glass forming melts. Shear in the melt can be reduced in low-g, thus enhancing undercooling and glass formation.

The viscosity of a model glass (lithium di-silicate, L2S) often used for crystallization studies has been measured at very low shear rates using a dynamic mechanical thermal analyzer. Our results are consistent with increasing viscosity with a lowering of shear rates. The viscosity of L2S may vary as much as an order of magnitude depending on the shear rate in the temperature region of maximum nucleation and crystal growth. Classical equations for nucleation and crystal growth rates, are inversely related to the viscosity and viscosity to the third power respectively. An order of magnitude variation in viscosity (with shear) at a given temperature would have dramatic effects on glass crystallization

Crystallization studies with the heavy metal fluoride glass ZBLAN ($\text{ZrF}_2\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) to examine the effect of shear on crystallization are being initiated. Samples are to be melted and quenched under quiescent conditions at different shear rates to determine the effect on crystallization.

The results from this study are expected to advance the current scientific understanding of glass formation in low-g and glass crystallization under glass molding conditions and will improve the scientific understanding of technological processes such as fiber pulling, bulk amorphous alloys, and glass fabrication processes.

Introduction

The heavy metal fluoride glasses represent a class of reasonably good glass forming compositions with very unique infrared optical properties that have been of interest to researchers for 20 years.¹ The most extensively studied glass with the most potential for practical applications is ZBLAN, which contains

Keywords: shear thinning, glass, ZBLAN, glass formation, low gravity, new research

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the fluorides of zirconium, barium, lanthanum, aluminum, and sodium. It has a broad transmission range (0.3-6 μ m), low index of refraction ($\sim$ 1.43), low dispersion, low Raleigh scattering, ultra-low thermal dispersion, and potential ultra-low signal attenuation². Potential applications include fiber amplifiers, fiber optic gyroscopes, delivery systems for laser cutting, drilling and surgery, radiation resistant data links, nonlinear optical systems, and ultra-low-loss repeater-less transcontinental and transoceanic optical fiber. Potential markets for these materials are in the tens of billions of dollars per year³.

Optical fiber from this material has excellent transmission characteristics in the IR, but the glass is somewhat susceptible to nucleation and crystallization. The theoretical intrinsic loss coefficient for ZBLAN at 2 microns is 0.001 dB/Km. Extrinsic losses, however, cause significant attenuation. The lowest loss coefficient measured is 0.7 dB/Km. This compares with the loss coefficient for fiber optic grade fused silica glass of 0.2 dB/Km. The extrinsic losses in ZBLAN have been attributed to 1) impurities which might be lowered by containerless processing and 2) to scattering from micro-crystallites that form during glass preform production or during fiber drawing. Finding a way to better control and eliminate these nuclei could have a very significant impact on the billion dollar information fiber optic industry.

A number of experiments have been performed with glass forming materials in space that provide evidence of enhanced glass formation for glasses prepared in space. These experiments have been of two types, crystallization studies and diffusion studies.

In general, the glasses have been shown to have much more homogeneous compositional distribution⁴ than terrestrial samples and the glasses have been shown to be more resistant to crystallization^{5,6}.

Two groups have reported that the crystallization of ZBLAN is reduced by processing in low-g^{2,7}. The ZBLAN fiber in the figure on the left of Figure 1, was heat treated on Conquest-1 sub-orbital rocket flight. Its glassy nature is indicated by the smooth surface (a line of bubbles formed where it contacted the container). By contrast, the ZBLAN fiber on the right of Figure 1 was heated on Earth under identical conditions, showing a great deal of crystallization.

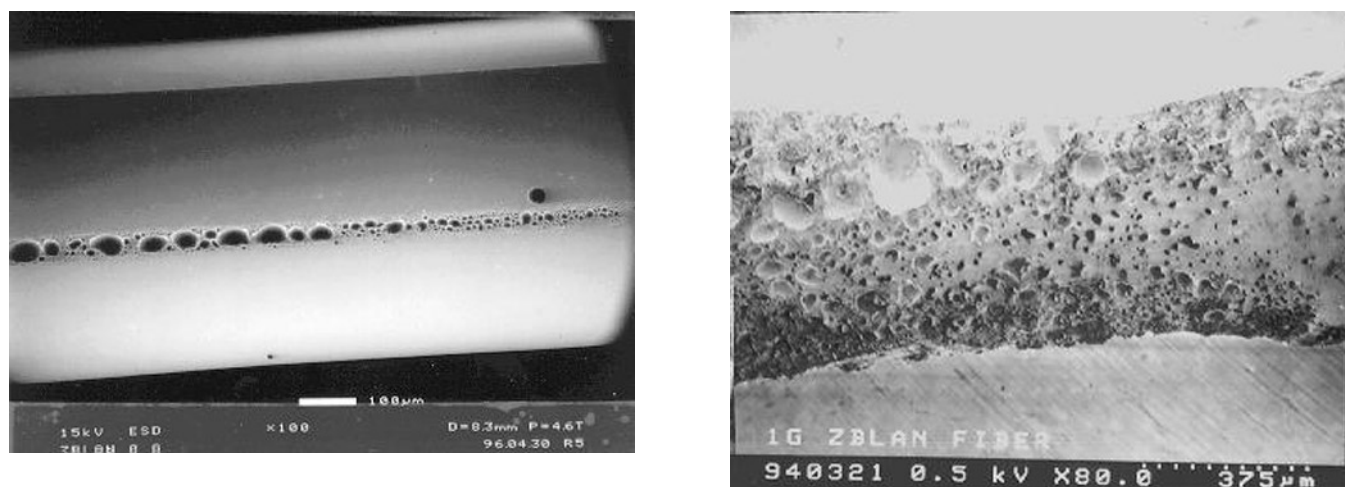


Figure 1. On left, ZBLAN fiber heated in a low-g rocket experiment with essentially no crystallization. On the right, ZBLAN fiber heated in 1-g with excessive crystallization.

Theory

Shear Thinning is the reduction of viscosity when a fluid flows. Fluids exhibit much lower flow rates in low-g than in 1-g. If the glass exhibits shear thinning, then the viscosity will be higher in low-g than in 1-g. One can predict the effect of shear thinning on crystallization.⁸ Viscosity is the only directly measurable kinetic parameter used in crystal nucleation and growth equations. In the classical treatment of crystallization⁹ nucleation rate, I , and crystal growth rate, U , are both inversely proportional to viscosity, η , with the viscosity term appearing in the pre-exponential factor.

$$I = (k_n/\eta) \exp[-b\alpha^3\beta T_m/T(1-T_r)^2]$$
$$U = (k'_n/\eta) [1-\exp(-\beta(T_m-T)/T)]$$

Where T_m is the melting temperature, T is the absolute temperature, and T_r is the reduced temperature. The kinetic constants k_n and k'_n , shape factor, b , and dimensionless parameters related to the liquid-crystal interfacial tension, α , and entropy of fusion, b .⁹

The fraction of glass crystallized, X , with time at a given temperature¹⁰ is a function of the rate of nucleation, the third power of the growth rate, and the fourth power of time.

$$X = (\pi/3)(IU^3t^4)$$

Under conditions of shear thinning, the effective viscosity decreases with increasing shear rate so that the viscosity can be expressed as a function of shear rate, $\eta(\dot{\epsilon})$. The crystallization parameters such as the nucleation rate will also be a function of shear rate.

$$I(\dot{\epsilon}) = (k_n/\eta(\dot{\epsilon}))\exp[-b\alpha^3\beta T_m/T(1-T_r)^2]$$

Low g-processing is known to greatly reduce convection, which reduces shear in the liquid. This would reduce any shear thinning in the liquid subsequently increasing the viscosity of the liquid, thereby reducing nucleation and growth rates. For an increase in viscosity by a factor of 2, the nucleation and growth rates each are reduced by half, but the fraction crystallized is reduced by a factor of 16. Since shear in liquid occurs as a result of fluid flow and fluid flow is greatly reduced in low gravity, we have crystallization equations which are affected by gravitational effects.

A number of glass forming liquids have been shown to exhibit shear thinning with an order of magnitude lowering of the viscosity. This is attributed to structural rearrangements in the liquid, and in particular to the orientation of chain like flow units¹¹. In phosphate melts, evidence of anisotropic behavior in sheared glass melts is indicated at viscosities less than 10^6 poise, being attributed to the “orientation of the phosphate tetrahedra chains”¹². Shear thinning in lower viscosity liquids is indicated by molecular dynamics studies of a simple Lenard-Jones liquid consisting of spherical hard spheres. A tendency of the molecules to order themselves into layers parallel to the flow was shown.¹³

At low shear rates, the viscosity of a number of polymer melts increases rapidly at low shear rates due to shear thinning. In order to calibrate our instrumentation, we prepared a known shear thinning liquid composed of the polymer PIB in mineral oil.¹⁴ As one can see from Figure 2, at the lowest measured shear rates the viscosity increases very rapidly with decreasing shear rate.

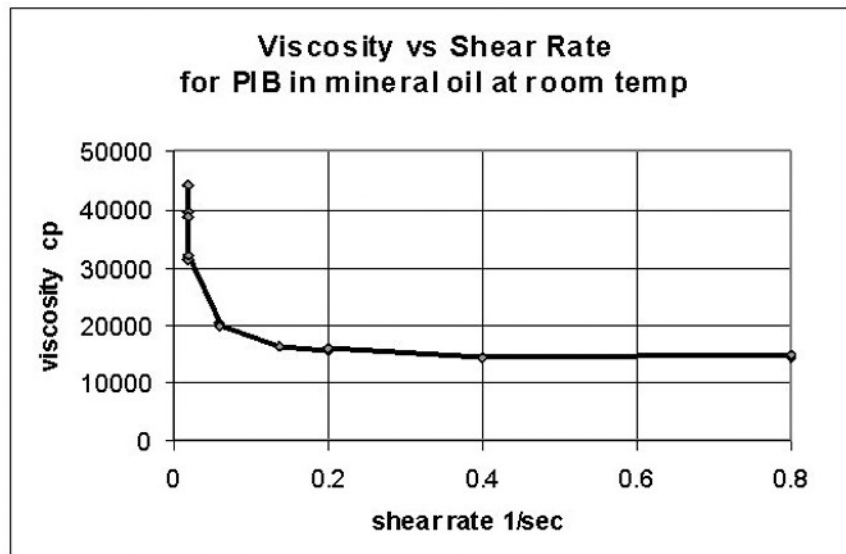


Figure 2. Viscosity vs. shear rate for 6% PIB, polyisobutylene, dissolved in mineral oil.

It is known that flow in undercooled polymer melts initiates crystallization¹⁵. It is also known that extrusion processing of glass-ceramic glass-forming melts catalyses the nucleation and growth of crystals¹⁶. Relatively high growth and nucleation rates have been reported in lithium di-silicate melts extruded at 540C where steady state nucleation and growth are practically zero for non-stressed samples⁸. Even though under most conditions glasses exhibit Newtonian viscous flow, non-Newtonian viscous flow has been reported at high strain rates in highly viscous melts^{17,18}.

Experiments

A vacuum glovebox has been setup to perform crystallization studies of ZBLAN under very high purity atmospheric control, see Figure 3. The vacuum chamber can be evacuated and backfilled with high purity gas, and then an access door opened to provide access with a glove to the experiment. Experiments are being performed with samples under shear stress, in order to determine the effect of shear on nucleation and crystallization.

A rapid thermal analyzer system developed by the PI¹⁹ has been redesigned to examine the crystallization of ZBLAN. The system involves a suspended sample on a Pt thermocouple which is rapidly heated by a halogen lamp controlled by a computer controlled power supply, see Figure 4. Sample temperatures are measured and the system is controlled by Labview software. Because of the low thermal mass of the system, it is suitable for collection of thermal data at rapid heating and cooling rates. It has been utilized for studies of the heterogeneous nucleation of reluctant glass formers²⁰. Data will be collected for a range of heating and cooling rates. The time and temperature dependence of transformation and the critical cooling rate under different shear conditions can be determined from the quenching data.

The viscosity of ZBLAN is fairly well characterized over the undercooled temperature range with data from around the melting temperature, around the glass transition temperature, and some measurements in the intermediate range. It has been assumed that the liquid is Newtonian over the entire range. We are developing the methods to measure the viscosity at different shear rates to determine if shear thinning

occurs in ZBLAN melts at low shear rates. A Rheometrics, Inc. DMTA V has been purchased to perform viscoelastic measurements on ZBLAN, see Figure 5.

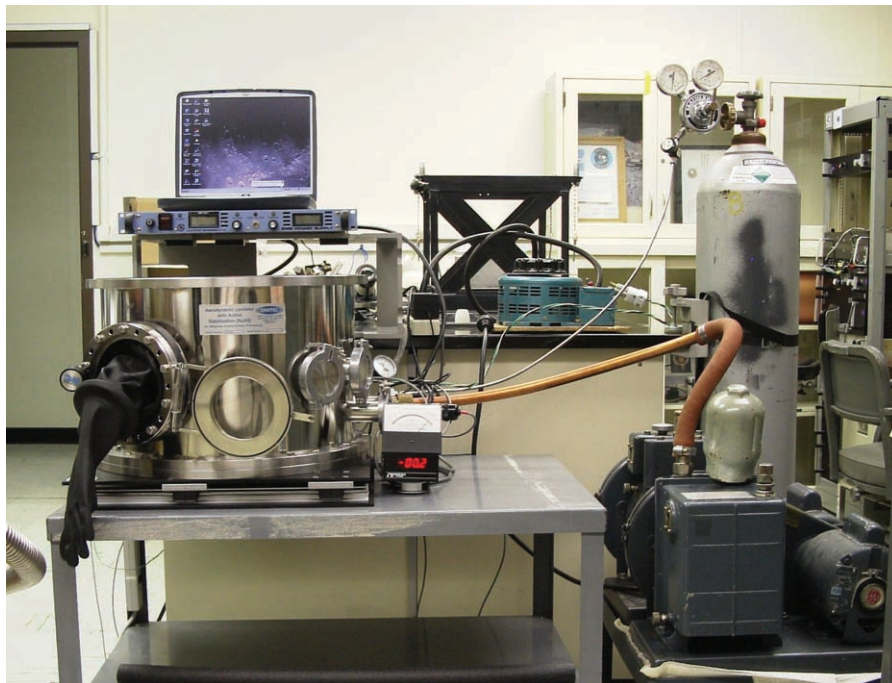


Figure 3. High purity atmosphere control vacuum glovebox.

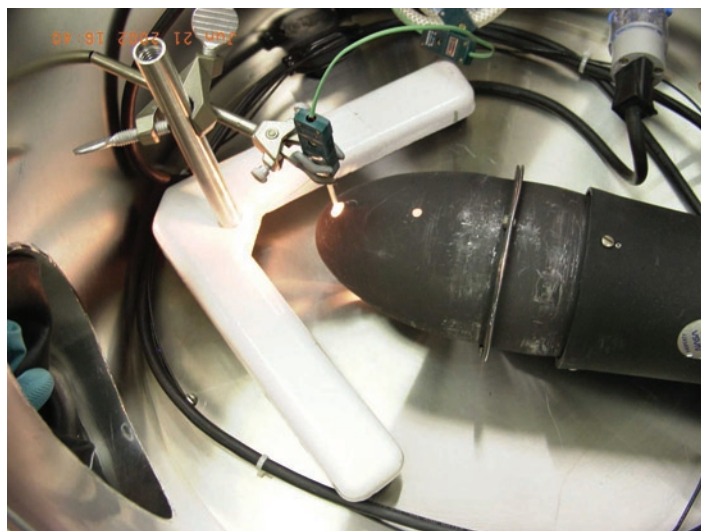


Figure 4. Ellipsoid lamp furnace.

This high temperature Dynamic Mechanical Thermal Analyzer, DMTA, can perform controlled shear, controlled stress, and dynamic viscoelastic measurements on liquids and glasses. Because of certain heat loss problems, it is being redesigned to perform the controlled shear and controlled stress experiments on viscous fluids for viscosity measurements at high temperatures without excessive heat loss, see Figure 6.

Parallel Plate Rheometry is being used to determine the viscosity of glass at very low shear rates. Figure 7 illustrates the test fixture. A constant force squeezes the glass sample. Viscosity is determined from the rate of motion of the parallel plate^{21,22}.



Figure 5. Rheometric, Inc. DMTA V

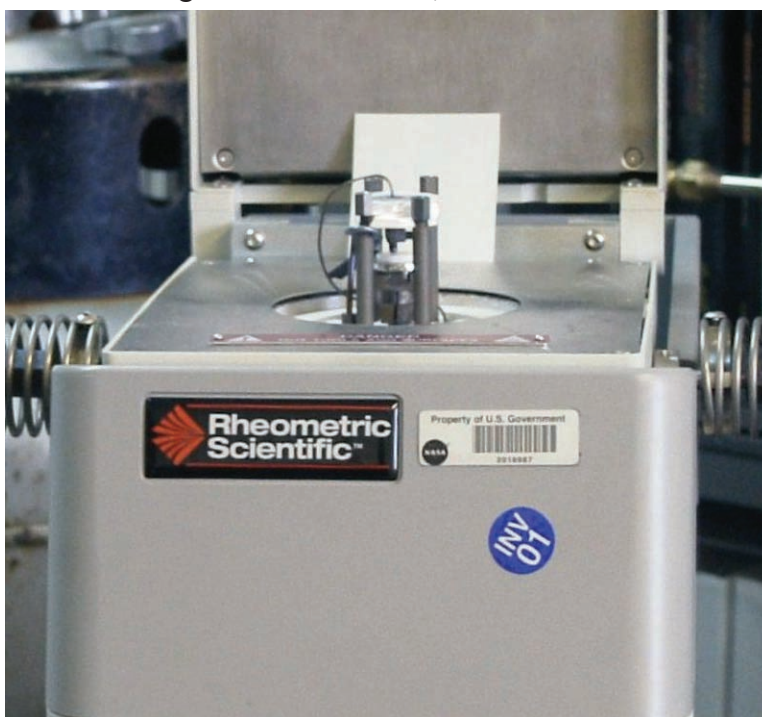


Figure 6. Inside of the DMTA showing the test fixture raised from the furnace.

Lithium di-silicate has been used as a test model material for initial viscosity measurements. Samples were provided by Dr. Delbert Day from the University of Missouri, Rolla. A constant load was applied to the glass and the sample was heated to a controlled temperature. The rate of deflection of the squeezing plates was measured. Data from 4 temperatures is shown in Figure 8.



Figure 7. DMTA test fixture for parallel plate viscosity measurements.

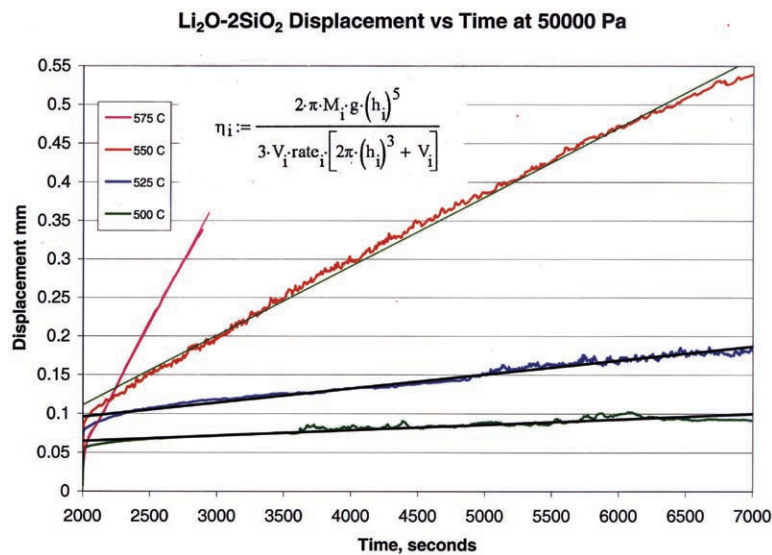


Figure 8. Deflection plots for 4 temperature experiments for Lithium di-silicate glass.

Calculated values for the viscosity are plotted on the graph of Dr. Day's collection of viscosity data from the literature, see Figure 9. The data is above the curve fit to published experimental data. This is consistent with reduced shear thinning in these current measurements, since the shear rate with this parallel plate measurement method is much lower than other measurement methods. The actual glass temperature for these 4 data points is not known as precisely as we would like at this time. We now know that there is significant heat loss through the displacement sensor that lowers the sample temperature by an unknown amount. The sample fixture arrangement is being redesigned to reduce heat loss providing more isothermal experimental conditions. A sample temperature sensor is also being added to the instrument to measure the temperature directly.

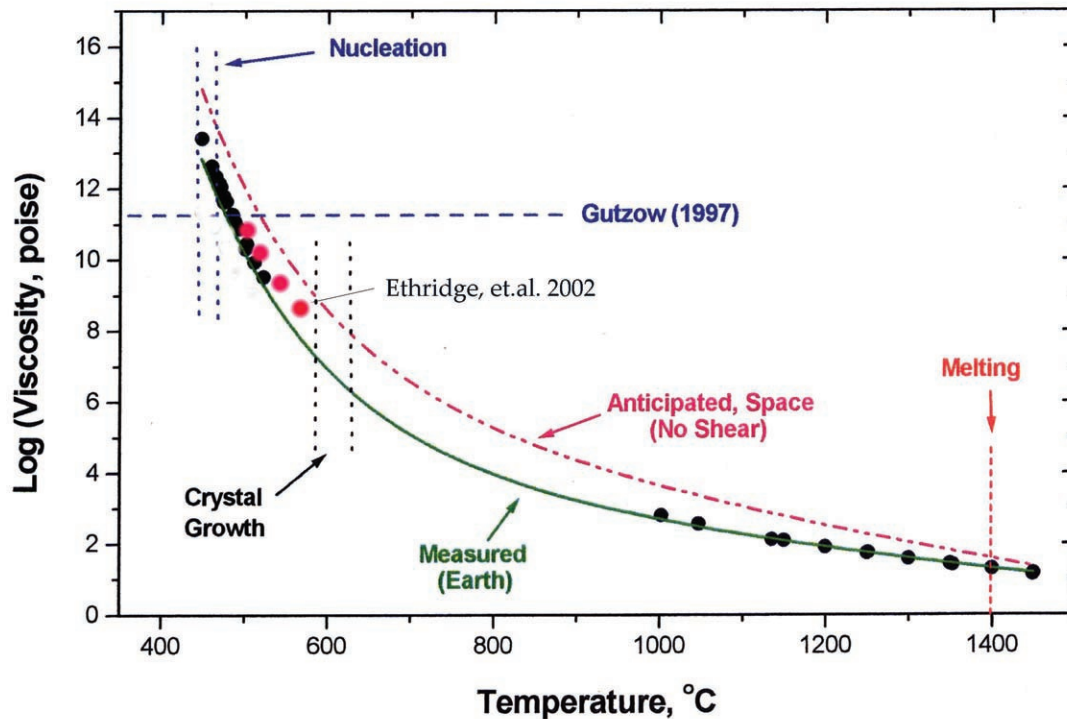


Figure 9. Lithium di-Silicate viscosity data for 4 temperatures, determined from parallel plate viscometry methods plotted on a figure from Dr Delbert Day's Science Concept Review, containing a compilation of data from the literature.

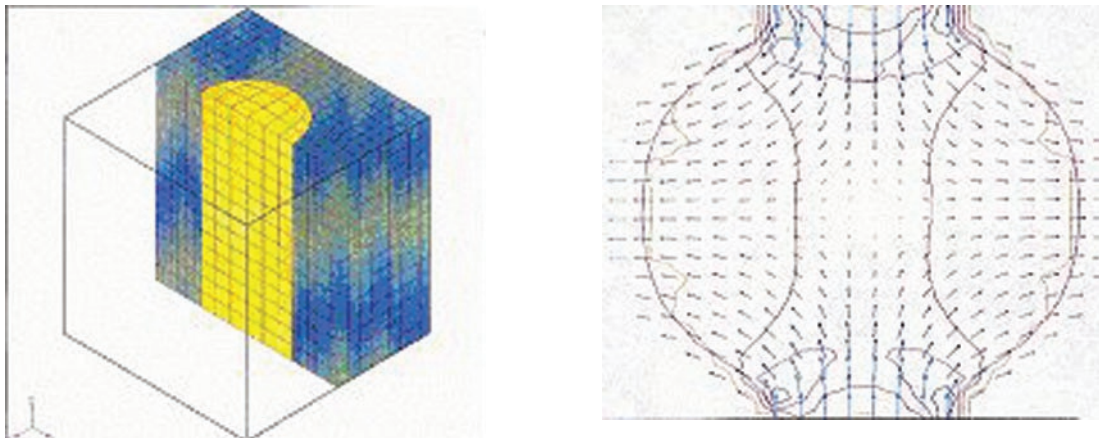


Figure 10. FIDAP fluid dynamic calculations of parallel plate viscometry.

Knowledge of the shear rate in the sample during the viscosity measurement is very important for this study. The experiment is being modeled by Dr. Basil Antar utilizing FIDAP software. The parallel plate squeeze flow experiment used for the above measurements has been modeled by inputting the experimental conditions on the sample, utilizing known materials properties, and the measured viscosity. Flow velocities and shear rates in the viscous liquid are being calculated, see Figure 10. This work will continue with more viscosity measurements and characterization of the shear rates within the samples.

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INVESTIGATION OF THE CRYSTAL GROWTH OF DIELECTRIC MATERIALS BY THE BRIDGMAN TECHNIQUE USING VIBRATIONAL CONTROL

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Fluid convection is an important phenomenon in crystal-melt systems. When uncontrolled, it can lead to a variety of problems including the incorporation of defects into a growing crystal. In a microgravity environment, where solutal and thermal convection is minimal, g-jitter, random vibrations produced from various sources, has been found to cause undesirable fluid flow. One potential solution to this problem involves the introduction of precisely controlled convection to suppress these flows. Forced convection is already used in many earth-based crystal growth processes to improve crystal quality and growth rates by either inducing or suppressing the naturally occurring convection.

This research program has focused on convection induced through the application of low-frequency vibrations, either directly into the melt with a vibrating disk (applied vibrational control [AVC]), or external to the growth ampoule (coupled vibrational stirring [Both vibrational techniques produce significant convection, and the benefits/drawbacks of each technique will be discussed.

A water/glycerin system was used to determine important vibrational parameters and to make quantitative measurements of fluid flow produced through vibrations. Fluid flow was imaged with the aid of tracer particles. Important dependent variables such as fluid velocity profiles were measured as a function of vibrational settings, crucible geometry, and fluid properties.

The influence of vibrational flow was investigated in NaNO₃, a low temperature (306°C) growth system that could be directly observed with the aid of a transparent furnace. Effects on growth rate, interface shape and position, and doping profiles were observed. The effect of these techniques was also examined in high temperature systems (lead magnesium niobate-lead titanate for CVS and lead telluride for AVC).

Keywords: crystal growth, vibrations, fluid flow, convection, new research

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FLIGHT PLANNING FOR THE INTERNATIONAL SPACE STATION - LEVITATION OBSERVATION OF DENDRITE EVOLUTION IN STEEL TERNARY ALLOY RAPID SOLIDIFICATION (LODESTARS)

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Abstract

During rapid solidification, a molten sample is cooled below its equilibrium solidification temperature to form a metastable liquid. Once nucleation is initiated, growth of the solid phase proceeds and can be seen as a sudden rise in temperature. The heat of fusion is rejected ahead of the growing dendrites into the undercooled liquid in a process known as recalescence.

Fe-Cr-Ni alloys may form several equilibrium phases and the hypoeutectic alloys, with compositions near the commercially important 316 stainless steel alloy, are observed to solidify by way of a two-step process known as double recalescence. During double recalescence, the first temperature rise is associated with formation of the metastable ferritic solid phase with subsequent conversion to the stable austenitic phase during the second temperature rise. Selection of which phase grows into the undercooled melt during primary solidification may be accomplished by choice of the appropriate nucleation trigger material or by control of the processing parameters during rapid solidification. Due to the highly reactive nature of the molten sample material and in order to avoid contamination of the undercooled melt, a containerless electromagnetic levitation (EML) processing technique is used.

In ground-based EML, the same forces that support the weight of the sample against gravity also drive convection in the liquid sample. However, in microgravity, the force required to position the sample is greatly reduced, so convection may be controlled over a wide range of internal flows. Space Shuttle experiments have shown that the double recalescence behavior of Fe-Cr-Ni alloys changes between ground and space EML experiments. This program is aimed at understanding how melt convection influences phase selection and the evolution of rapid solidification microstructures.

Introduction

Suppression of convection in microgravity has been shown to dramatically impact rapid solidification kinetics. Glicksman and Huang¹ observed that the orientation of the g-vector relative to the principal growth direction could affect both growth velocity and side branch morphology during dendritic growth of succinonitrile, a non-metallic analog system.

The effect of convection on nucleation has not been similarly demonstrated. The purpose of this program is to develop a database characterizing the transformation from ferrite to austenite in Fe-Cr-Ni alloys to understand of the effects of convection on time-dependent nucleation phenomena during rapid

Keywords: rapid solidification, recalescence, convection

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solidification from the melt. A ternary alloy system was chosen so that varying the composition allows independent control of thermal and solutal effects.

This research has application to the design of industrial welding, spray forming and strip casting operations for a commercially important class of structural materials. In addition, this research also addresses fundamental issues relating to rapid solidification behavior, metastable phase selection and analysis of the processes governing microstructural evolution. By mapping out how convection influences nucleation behavior we hope to provide insight into how to better control solidification structures. Experiments focus on the use of convection as a processing control parameter.

Background

Classical nucleation theory predicts that the time-dependent nucleation rate, I_t , is a function of the steady-state nucleation rate, I_s :

$$I_s = N k_n^+ Z \exp \left(-\frac{\Delta G_n}{k_B T n_c^2} f(\theta) \right) \quad (1)$$

$$I_t = I_s \exp \left(-\frac{\tau}{t} \right) \quad (2)$$

N is the number of nucleation sites, k_n^+ the rate of monomer addition to the critical nucleus, Z the Zeldovich factor with $Z = [\Delta G_n / 3 \pi k_B T]^{1/2}$, ΔG_n the free energy of formation for the critical nucleus, k_B the Boltzmann constant, T the nucleation temperature, n_c the number of atoms in the critical nucleus, the contact angle factor $f(\theta) = 1/4 (2 + \cos \theta)(1 - \cos \theta)^2$, t the time and τ the characteristic incubation time². Kantrowitz proposed an expression including the atomic diffusivity D :

$$I_t = 2N \left(\frac{D}{\pi t} \right)^{1/2} \exp \left(-\frac{n_c^2}{D t} \right) \quad (3)$$

valid for small times such that the time dependent nucleation rate is not appreciable until :

$$\tau = \frac{n_c^2}{D} \quad (4)$$

in agreement with Turnbull³ for diffusivity across a liquid interface and with Russell⁴ who introduced a factor of ten to correct for intrinsic bulk diffusivity during solid state transformations. Recent work by Kelton⁵ has shown that the time-dependent nucleation rate is significantly longer in partitioning transformations when the interfacial attachment and diffusive transport are linked in a coupled-flux analysis approach. By including the effects of solute diffusion in nucleation theory, a theoretical framework is established to test how convection may influence transient nucleation phenomena.

Based on classical nucleation theory, the number of atoms in the critical nucleus is a function of the geometry of the process. Comparing a spherical nucleus to that for a cylindrical flat plate :

$$n_c^{sphere} = \frac{4}{3} \pi r_c^3 \propto \frac{C_{sphere}}{(\Delta T)^3} \quad (5)$$

$$n_c^{plate} = \pi r_c^2 \propto \frac{C_{plate}}{(\Delta T)^2} \quad (6)$$

for a critical nucleus radius of $r_c = \frac{2 \gamma T_m}{\Delta H (\Delta T)}$ with γ the surface energy, T_m the melting point, ΔH the heat of fusion, and ΔT the undercooling. Combining these results we see that for a spherical cap the characteristic delay time should be proportional to the undercooling to the negative sixth power while for a cylindrical flat plate the delay should be proportional to the undercooling to the negative fourth power.

Fe-Cr-Ni alloys may form several equilibrium phases and the hypoeutectic alloys, with compositions near the commercially important 316 stainless steel alloy, are observed to solidify by way of a two-step process known as double recalescence, shown in Figure 1. During double recalescence, the first temperature rise is associated with formation of the metastable ferritic solid phase with subsequent conversion to the stable austenitic phase during the second temperature rise^{6,7}. This experimentally determined delay time is assumed to be analogous to the theoretically evaluated incubation time.

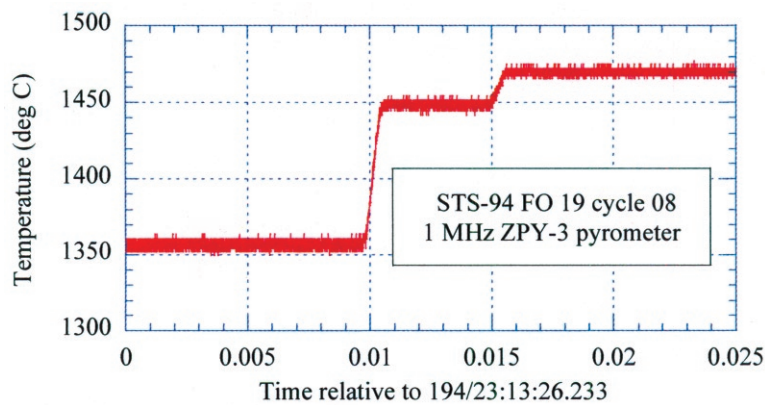


Figure 1. Double recalescence in ternary steel alloys processed in microgravity.

Ground-based research on levitation melted samples and on rapidly solidified atomized droplets has shown the strong influence of processing conditions on the selection between bcc-ferrite (delta) and the fcc-austenite (gamma) in Fe-Ni and Fe-Cr-Ni alloys. Early work on metastable formation in Fe-Ni alloys was accomplished by investigation of the solidification behavior of fine powders including the work of Cech⁸ and Thoma and Perepezko⁹. Similar behavior was seen for commercial alloys both by Kelly and VanderSande for gas-atomized type 303 stainless steel¹⁰ and by MacIsaac et al. in type 316 stainless steel¹¹ cooled in a glass matrix. The metastable phase formation was identified using a metallographic technique.

Solute-rich inversely cored structures in glass-encased bulk samples of Fe-Ni alloys were reported by Kattamis and Flemings¹² and Perepezko et al.¹³ Remelting and coarsening during and immediately after recalescence was proposed by Abbaschian and Flemings¹⁴ as mechanisms to explain the observed microstructure especially if the cooling rate was high¹⁵. The solidification path involved diffusionless rapid solidification to the equilibrium solidus or to the T_o -curve, a subsequent temperature rise to the completion of recalescence as described by the equilibrium phase diagram, and finally a decrease in temperature during slow equilibrium cooling. Coarsening defines the final observed dendrite arm spacing.¹²

At first, these inversely cored structures were assumed to represent the portion of solidification where solute trapping was important during the first rapid recalescence period but pyrometric evidence^{6,16} and

metallographic evidence combined with concentration mapping of quenched steel samples by Koseki and Flemings^{7,17} showed retention of the metastable bcc phase as shown in Figure 2. Calculations confirmed that the ferrite phase was more likely to nucleate from the melt based on differences in liquid-solid surface energy.



Figure 2. Retained metastable bcc core within fcc dendrites following rapid quenching of double recalescence in containerless processing of steel samples⁷.

During double recalescence, both the intermediate temperature increase following primary recalescence and the delay between events is seen to be a strong function of composition. In separate investigations, Koseki and Flemings⁶, Loser¹⁸, Moir¹⁹ and Volkmann²⁰⁻²² documented the relationship between growth kinetics, undercooling and composition.

Stainless steel alloys require special handling in order to achieve a significant undercooling range. In particular, chromium is particularly susceptible to contamination through reaction with crucible material. When attempting to perform rapid solidification tests, the formation of active heterogeneous nucleation sites limits the undercooling that may be achieved. A containerless technique minimizes this contamination.

Electromagnetic levitation (EML) is attractive as an experimental tool in these types of investigations because significant convection may be introduced into the melt²³. The sample is positioned in the electromagnetic potential well generated by alternating current flowing through water-cooled copper coils. The eddy currents induced in the sample produce heat and levitate the sample. Induced currents also interact with the applied magnetic field to produce stirring forces inside the molten sample which lead to intense internal agitation, mixing and surface deformation. Quantification of induced flows is accomplished by magnetohydrodynamic modeling. Also, varying the sample size varies the Reynolds number independent of the absolute maximum melt recirculation velocity.

The same electromagnetic forces that position the sample also drive internal flow within the droplet. Since the electromagnetic force balances the weight of the sample, only a narrow range of convective conditions is accessible in 1-g EML. However, in microgravity, the positioning forces required to contain the sample are significantly weaker than on ground allowing the attainment of lower internal flow conditions. High force, high flow conditions may also be selected in microgravity and thus a wide range of convective environments may be accessed.

Previous testing in microgravity during the MSL-1 shuttle mission showed significant difference from the solidification behavior observed in ground-based EML experiments. Although growth rate measurements show no significant difference in behavior, the delay between primary recalescence and nucleation of the stable phase was approximately four times longer in microgravity^{24,25} as shown in Figure 3. Data points taken during MSL-1R are shown in red and compared to results obtained in ground-based EML experiments both at MIT and at IFW-Dresden as shown in blue. This deviation was attributed to differences in convection conditions encountered on ground and in microgravity.

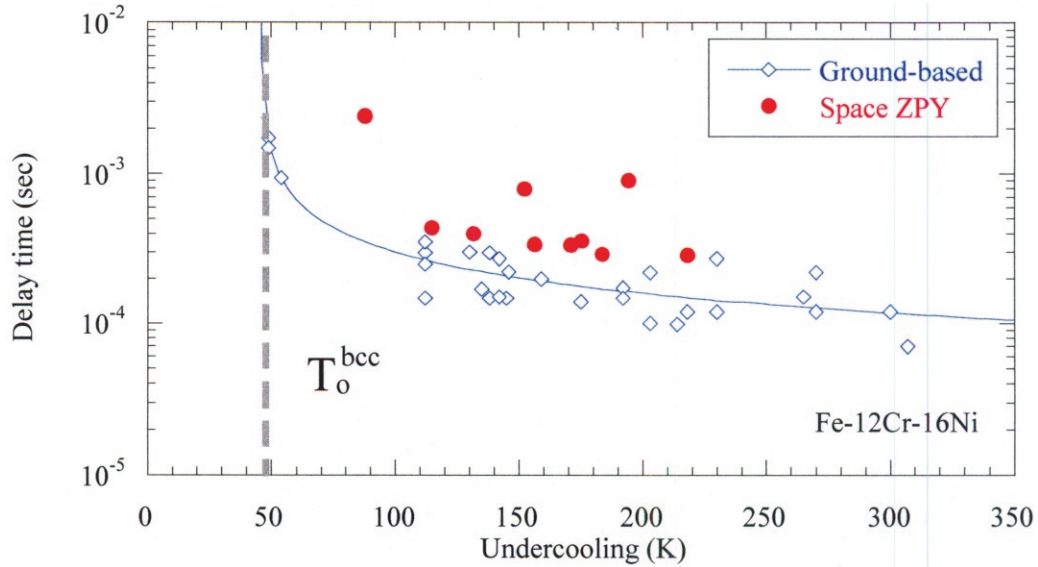


Figure 3. Delay between recalescence events.

Flight Preparations

Evaluation of Thermodynamic Driving Force

In a binary alloy system, solute concentration and corresponding thermal driving force which controls subsequent transformations are set by the equilibrium phase diagram. If a ternary alloy is used, the solute composition may be carefully adjusted to yield the same thermal driving force for different solute concentrations. Kertiz²⁶ is investigating the growth of the stable phase into the metastable array in ground-based investigations. The equilibrium phase diagram, metastable phase diagram and thermodynamic properties can be evaluated over the entire family of ternary alloys using the software package ThermoCalc (Royal Institute of Technology, Stockholm Sweden). From these results, the thermal driving force may be approximated as the difference in T_o temperatures for each phase (since this represents the temperature difference between metastable and stable phases, or undercooling, following primary recalescence).

$$\Delta T_o = T_o^{fcc} - T_o^{bcc} \quad (7)$$

As shown in the left side of Figure 4, the right side of the figure presents two isopleth sections of the calculated metastable phase diagram. The figure shows how alloys of dissimilar constitution may be selected to obtain similar thermal driving forces; this ability to isolate effects of solute and thermal driving forces is the key attribute for selection of a ternary alloy system.

As shown in Figure 5, a plot of the delay times for various alloys as a function of the thermal driving force ΔT_o shows a slope of $m = (-4.0)$ indicating that nucleation of the stable phase occurs as a flat plate on the pre-existing metastable skeleton.

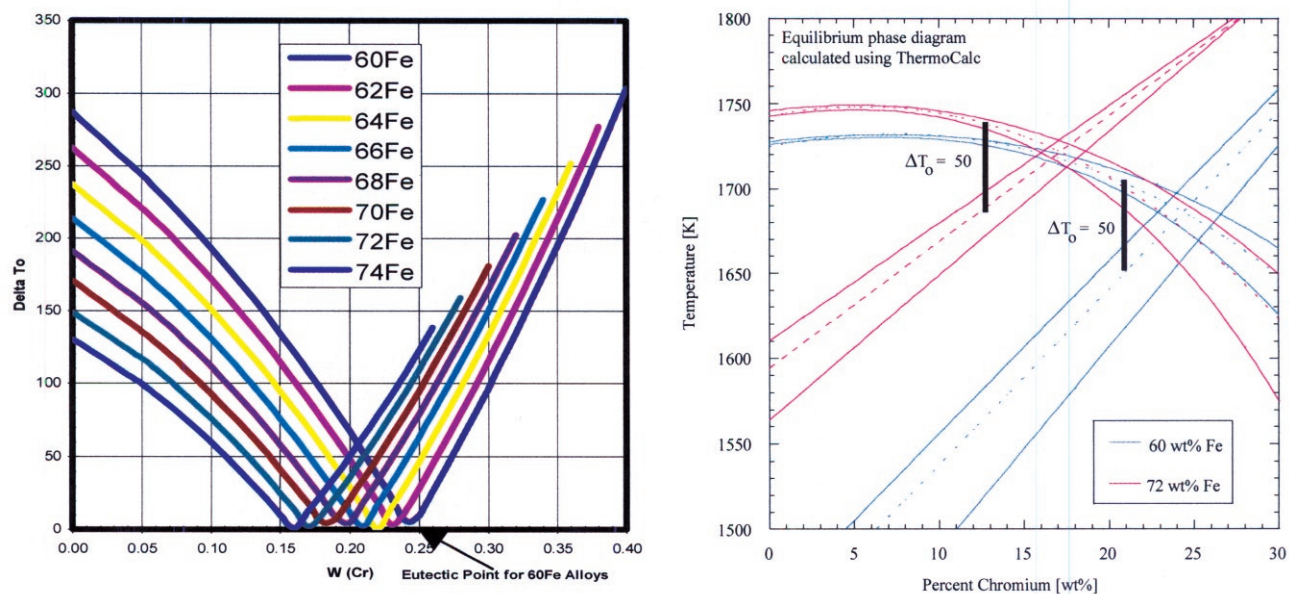


Figure 4. Thermal driving force and alloy selection.

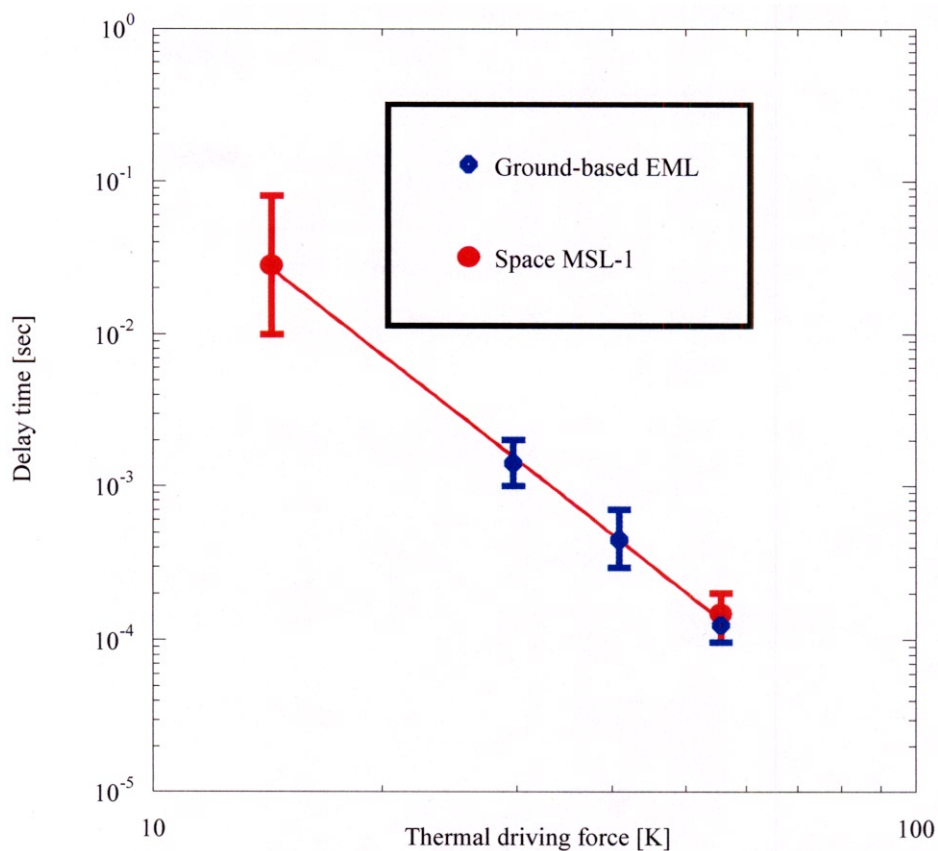


Figure 5. Thermal driving force and delay time; the bars show the variation due to convection and to the initial undercooling which determines the initial fraction solid.

Electromagnetic Levitation (EML) Testing

EML testing as part of ongoing thesis work at MIT by Kensel²⁷ has shown that alloys with similar thermal driving force have similar delay time behavior. Figure 6 shows that the alloys with 50 degree driving force (as depicted in Figure 4) have comparable delay times. The general shape of this curve can be predicted from classical nucleation theory when combined with a simplified model of how rapid solidification progresses as a function of undercooling. In this model, undercooling during primary solidification results in a defined quantity of metastable fraction solid as predicted by the Stefan equation:

$$f_s^\delta \Delta H_{bcc} = C_p \Delta T_\delta \quad (8)$$

where f_s^δ is the fraction solid of the primary metastable delta-phase, ΔH_{bcc} the latent heat of fusion, C_p the heat capacity and ΔT_δ the undercooling relative to the metastable phase diagram.

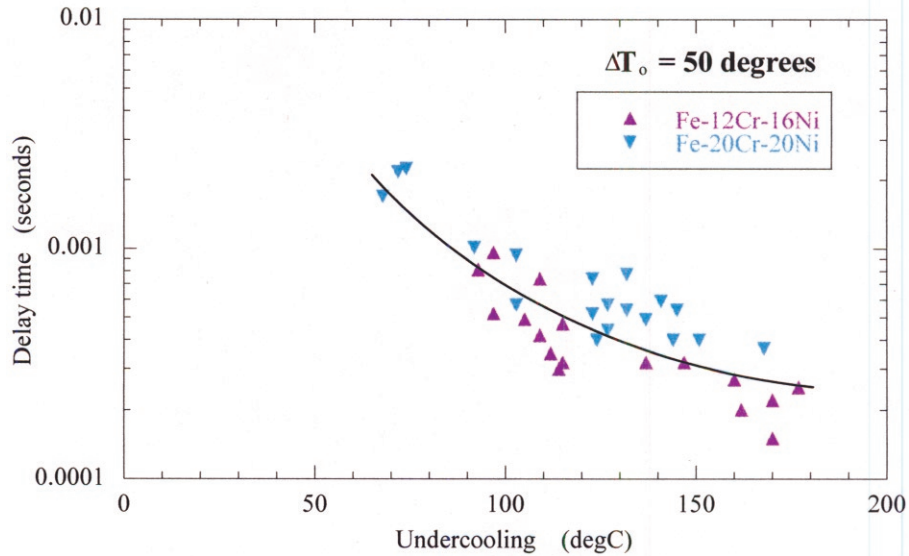


Figure 6. Delay time as a function of undercooling.

From the equilibrium phase diagram, the lower the initial undercooling, the lower the fraction solid that must result, and the higher the primary recalescence temperature (from application of the lever rule). This effect will be pronounced at low undercoolings but as primary undercooling is increased and growth velocity for the metastable phase becomes rapid, deviation from the equilibrium phase diagram is expected.

Electrostatic Levitation (ESL) Testing

ESL testing at NASA Marshall Space Flight Center (MSFC) has centered on evaluating the delay behavior over the range of recirculation velocities accessible using Marangoni or surface tension driven flow. Since the ESL achieves containerless processing by imposing a voltage drop across the sample processing space and levitation occurs through electrostatic attraction (similar to classic experiments by R.A. Millikan on oil drops), the sample size for ESL testing is much smaller than that used in EML tests. ESL samples are around 1 mm in diameter while EML samples are between 6-10 mm. When the sample is free-cooled with the heating laser turned off, recirculation within the droplet quickly dampens to near zero velocity conditions.

In ESL processing, the cooling rate may be controlled by operating the heating laser at reduced power. Processing with the laser on also induces temperature differences across the sample surface and thus

surface tension driven flows result. ESL processing of Fe-Cr-Ni alloys gives laminar flow in the range of 0 – 6 cm/sec while EML processing on ground results in turbulent flow at about 32 cm/sec. Figure 7 shows a comparison between tests performed using the MSFC-ESL with the laser off and the laser on. The difference between the observed delay time for these two conditions is not statistically significant.

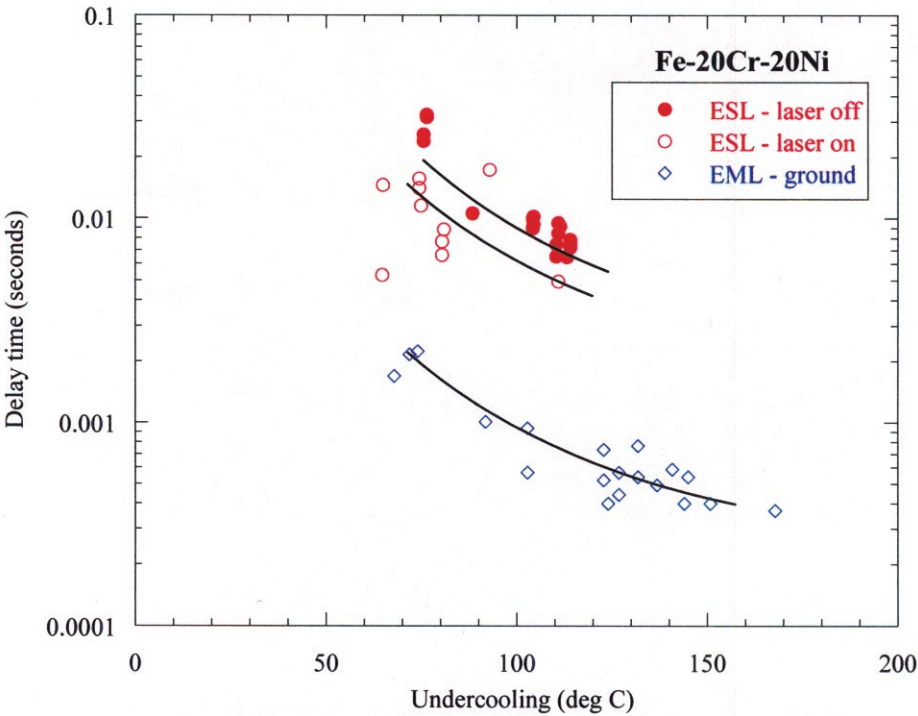


Figure 7. Comparing EML and ESL test results.

By comparison, ground-based EML testing on the same alloy composition yield results which vary significantly from the ESL delay times. All data sets show the same trend – delay times under high convective conditions are significantly shorter.

Justification for conducting experiments in microgravity

Due to the highly reactive nature of the molten sample material and in order to avoid contamination of the undercooled melt, a containerless processing technique must be used. Since the goal of the project is to investigate the role of convection in phase selection, we desire the ability to induce a range of known, steady-state levels of convection during rapid solidification processing. The range of flows to be explored must focus on the range of velocities between the extremes identified during the previous MSL-1 testing. Of particular interest is the behavior during transition from laminar to turbulent flow.

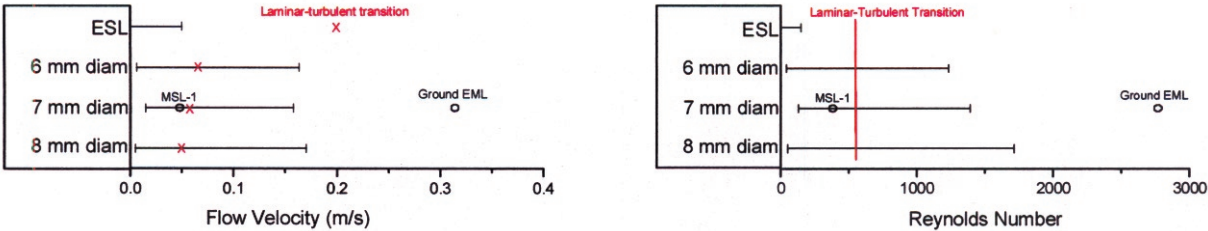


Figure 8. Comparison of the range of recirculation velocities and Reynolds numbers accessible using space- based EML to other experimental platforms²⁸.

Figure 8 shows a comparison of ground-based experimental platforms to that achievable using space-based EML. ESL testing can only access a laminar flow range from $0 < V_{\max} < 6$ cm/sec while ground-based EML is limited to turbulent flow corresponding to a condition where $V_{\max}$ is on the order of 32 cm/sec. Results from MSL-1 show that the significant change in nucleation behavior occurs between these two extremes (note that the ESL and MSL-1 results are of similar magnitude and correspond to laminar flow conditions). Only microgravity EML can access a majority of the full range and investigate the laminar/turbulent flow transition.

Summary

From high-speed digital images of the double recalescence behavior of Fe-Cr-Ni alloys in ground-based testing and in reduced gravity aboard the NASA KC-135 parabolic aircraft, we have shown that phase selection can be predicted based on a growth competition model. An important parameter in this model is the delay time between primary nucleation and subsequent nucleation of the stable solid within the liquid / metastable solid array. This delay time is a strong function of composition and a weak function of the undercooling of the melt below the metastable liquidus.

From the results obtained during the MSL-1 mission and in ground based electrostatic levitation testing at NASA Marshall Space Flight Center (MSFC), we also know that convection may significantly influence the delay time, especially at low undercoolings. We know that for ternary alloys with a similar thermal driving force, the nucleation delay is comparable; this contrasts with the observation that for a single alloy, different nucleation delays are seen under different convective conditions.

Currently, it is unclear what mechanism controls the formation of a heterogeneous site that allows nucleation of the austenitic phase on the pre-existing ferritic skeleton. By examining the behavior of the delay time under different convective conditions attainable in microgravity, we hypothesize that we can differentiate among several of these mechanisms to gain an understanding of how to control microstructural evolution.

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GRAVITATIONAL EFFECTS ON DISTORTION IN SINTERING

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Abstract

During sintering a powder compact gains strength through low-temperature interparticle bonding, usually induced by solid-state surface diffusion, followed by further strength contributions from high-temperature densification. In cases where a liquid phase forms, sintering densification is accelerated and shape retention is sustained while open pores remain and contribute capillary forces. Unfortunately, sintering densification requires the compact become thermally softened to a point where creep strain rates reach levels near 10^{-2} s^{-1} when the liquid forms. On the other hand, thermal softening of the powder compact substantially reduces the strength at high temperatures. Therefore, the *in situ* strength evolution during sintering is a primary focus to separate compact densification (as required for high performance) with minimized distortion (as required for net-shaping). With respect to gravitation effects on distortion during sintering there are two points of substantial weakness - prior to significant interparticle bonding and during final pore closure. This research is focused on understanding the competition among interparticle neck growth, densification, thermal softening, grain boundary wetting, capillary effects associated with liquid wetting and residual porosity, and gravity. Most surprising is the apparent role of gravity, where the deviatoric stress acting on the powder structure induces skeletal formation that reduces distortion. In contrast with theory, microgravity samples exhibit more distortion yet fail to fully densify.

Results are presented on the experimental concepts supporting an emerging model of sintering strength evolution that enables understanding of both distortion and densification. The experiments have relied on tungsten heavy alloys, various combinations of dihedral angle, pore size, initial porosity, liquid:solid ratio, and heating rates. On Earth, the dominant factor with respect to distortion is the starting body heterogeneity. Current modeling efforts are seeking some means to uniformly predict the distortion based on a starting pore structure heterogeneity parameter. Densification is largely unaffected by the initial pore structure, but distortion is highly variable, suggesting that nonuniform pore closure might be a significant parameter during sintering. With respect to flight experiments, plans include removal of the solid body forces acting on the solid grains, allowing stabilization of the pore structure and examination of the buoyancy effects with regard to distortion. In microgravity there is the surprising result that compacts do not densify, yet distort – a factor that is contrary to all current sintering models.

Densification without distortion during liquid phase sintering was achieved by manipulating microstructure and its evolution during sintering. Microstructure parameters such as the solid volume fraction, dihedral angle, initial porosity, and pore size were varied to measure densification and distortion behavior during LPS using W-Ni-Cu alloys. Green compacts were formed using ethylene-bis-stearamide as a pore-forming agent with the amount of polymer controlling the initial porosity. Different initial pore sizes were

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generated by varying the polymer particle size. Dihedral angle was varied by changing the Ni:Cu ratio in the alloys. Finally, the solid volume fraction was adjusted via the tungsten content. Distortion was quantified using profiles determined with a coordinate measuring machine to calculate a distortion parameter. Sintering results showed that solid volume fraction and dihedral angle are the dominant factors on densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and dihedral angle, while initial porosity and pore size have no observable effect on distortion at nearly full densification. Various strategies emerge to improve distortion control in liquid phase sintering.

Introduction

Liquid phase sintering is broadly used for net-shape manufacturing [1, 2]. In many systems the liquid enhances densification, since it provides a capillary force that pulls the solid grains together and offers a fast mass transport medium [3, 4]. However, liquid phase sintering is generally limited to high solid content compositions due to shape retention difficulties. In tungsten heavy alloys, the large density difference (over 10 g/cm³) between tungsten grains and the matrix (usually Ni, Cu, or Fe) induces tungsten grain settling along the gravitational direction, especially for liquid contents over approximately 25 vol.%, resulting in significant distortion [5, 6].

Densification has long been the subject of many investigations, and distortion has also been studied in recent works [5, 6, 7], but few reports have directly addressed distortion control. A systematic investigation of distortion is lacking. Similarly, the initial pore structure effects on distortion have been neglected and are still uncertain at this time. This work studies liquid phase sintering by investigating the microstructural effects on the combination of densification and distortion, including solid volume fraction, dihedral angle, green porosity, and green pore size. In this work, W-Ni-Cu tungsten heavy alloys with varying dihedral angles were liquid phase sintered and simultaneously monitored for densification and distortion. The sequence of densification and distortion during liquid phase sintering was investigated using quenching experiments. Processing strategies brought forth by this research aid in liquid phase sintering practice for the fabrication of high density and high precision components.

Experimental Procedures

The W-Ni-Cu tungsten heavy alloys with varying microstructures were fabricated from mixed powders. To control the green porosity and pore size, an organic binder, EBS (ethylene-bis-stearamide) was added to the powder mixture. During heating, the binder decomposed to leave pores in proportion to added concentration. Varying binder particle sizes created different green pore sizes. Dihedral angles were varied through the Ni:Cu ratio from 8:2 to 2:8. The initial formulations were adjusted to give final solid volume fraction (pore-free) ranging from about 60 to 85 vol.% using initial tungsten contents and the alloy balance being Ni and Cu.

The as-received tungsten powder was first deagglomerated by rod milling for 1 h in a 2000 cm³ plastic jar filled with argon. The ratio of rods to the powder was 10:1. The W, Ni, and Cu elemental powders were first mixed according to the target composition, and then mixed with the EBS binder at different particle sizes in a Turbala mixer for 20 min to achieve a homogenous distribution. The binder content in the mixture was in proportion to the desired green porosity.

The mixed powders were weighed and uniaxially die pressed at 175 MPa into cylinders 12.8 mm in diameter and 10 mm in height. The green compacts were heated to extract the binder at 550°C for 1 h in

dry hydrogen with dew point of -55°C . The hydrogen flow rate was 23 turnovers/h, and the heating rate was $3^{\circ}\text{C}/\text{min}$. After the binder was extracted, the compacts were weighed and measured again to calculate the green porosity.

Sintering was performed at 1480°C in a CM horizontal tube furnace in dry hydrogen with dew point of -55°C . The hydrogen flow rate was 35 turnovers/h. The heating rate was $10^{\circ}\text{C}/\text{min}$, and the holding time at sintering temperature was 30 min. To reduce oxidation, a 30 min hold at 1050°C was employed during heating.

Quenching experiments were employed to investigate the sequence of densification and distortion during liquid phase sintering. The 80W-16Ni-4Cu compacts with 67% green porosity were sintered at 1480°C in a CM vertical furnace in dry hydrogen atmosphere with dew point of -55°C . The hydrogen flow rate was 24 turnovers/h, heating rate was $10^{\circ}\text{C}/\text{min}$, and sintering holding times were from 0 to 30 min. After the sintering temperature and holding time were achieved, the samples were quenched into water at room temperature.

After sintering, distortion was quantified using a distortion parameter. Compact dimensions were first measured at various heights using a coordinate measuring machine (CMM). The measured sectional radii were normalized with respect to the maximum radius of the sintered compact. The distortion parameter equals the standard deviation of the normalized radii.

The densities of the sintered compacts were measured using water immersion method. Prior to measurement, the samples were infiltrated with light paraffin oil in a vacuum chamber for 15 min to fill all open pores.

Finally, the samples were sectioned along the longitudinal direction, mounted, and polished to a $0.05\text{ }\mu\text{m}$ finish for metallographic analysis. The solid volume fraction was measured manually by point-count method. Typically 3 micrographs were measured to ensure the statistical accuracy of $\pm 3\text{ vol.}\%$. Dihedral angle measurement was performed by manually measuring the angle between two connecting grains using a protractor. The median of 25 observations was reported as the true dihedral angle.

Experimental Results

All samples achieved nearly full density, except the sample with 90 wt.% W content which achieved only 94% of theoretical density. Solid volume fraction increased as initial tungsten content increased. Distortion decreased as initial tungsten content and solid volume fraction increased. The 80W alloy had the lowest solid volume fraction and most distortion, while the 90W alloy had the highest solid volume fraction and only showed slight distortion.

To investigate the dihedral angle effect on distortion, the solid volume fraction was constant by decreasing the initial tungsten content with decreasing Ni : Cu ratio (As Ni : Cu ratio decreases, W solubility in Ni-Cu matrix decreases). The alloys employed were 80W-16Ni-4Cu (Ni : Cu 8:2), 78.7W-12.8Ni-8.5Cu (Ni : Cu 6:4), 78W-11Ni-11Cu (Ni : Cu 5:5), 77.3W-9.1Ni-13.6Cu (Ni : Cu 4:6), and 75.6W-4.9Ni-19.5Cu (Ni : Cu 2:8). These alloys were liquid phase sintered at 1480°C for 30 min. The heating rate was $10^{\circ}\text{C}/\text{min}$. The initial green porosity was 36%, and the pore size was $87\text{ }\mu\text{m}$. The measured solid volume fraction was about 0.61 for all the samples. All the samples achieved a sintered density of above 95% of theoretical

density. The sintered density increased slightly as dihedral angle increased, except the 75.6W-4.9Ni-19.5Cu (Ni : Cu 2:8) alloy. Distortion decreased as the dihedral angle increased (Ni : Cu ratio decreased). The sample with dihedral angle of 46 degrees had the most distortion, while the sample with dihedral angle of 76 degrees did not distort.

A comprehensive study of porosity effect on distortion was conducted on three different tungsten alloys, 80W-16Ni-4Cu (Ni : Cu 8:2), 83W-13.6Ni-3.4Cu (Ni : Cu 8:2), and 90W-8Ni-2Cu (Ni : Cu 8:2). Compacts with different green porosities were sintered at 1480°C for 30 min. The heating rate was 10°C/min and the pore size was 87 μm . For the 80W-16Ni-4Cu alloy, all the samples with different green porosities achieved nearly full density and had similar distortion. The distortion parameter for the 80W-16Ni-4Cu alloy is about 0.38. For the 83W-13.6Ni-3.4Cu alloy, all the samples with different green porosities also achieved nearly full density and had similar distortion. The distortion parameter for the 83W-13.6Ni-3.4Cu alloy is about 0.11. The 80W-16Ni-4Cu alloy had more distortion than the 83W-13.6Ni-3.4 Cu alloy. Green porosity did not show observable effects on distortion of 80W and 83W alloys after nearly full densification. For the 90W-8Ni-2Cu alloy, samples with green porosities of 37% and 47% achieved nearly full density and showed slight distortion. Sample with green porosity of 57% achieved only 93% density, and sample with green porosity of 67% achieved only 88% density. Both samples retained shape.

All the samples with different pore sizes achieved a sintered density of above 96% of theoretical density, and had similar distortion parameter. Green pore size did not show significant effect on distortion.

For the 80W-16Ni-4Cu alloy, heating rate was adjusted while the green porosity and pore size were held constant. The compacts were heated to 1300°C at 10°C/min, and then the temperature was increased to 1480°C using 1, 3, 5, or 10°C/min heating rates. All of the samples achieved a sintered density above 96% of theoretical density. Distortion decreased as heating rate decreased. The sample with a 10°C/min heating rate had the most distortion, while the sample with a 1°C/min heating rate only showed slight distortion.

The experimental findings show distortion increased with increasing holding time, and distortion did not occur until after nearly full density was achieved. After sintering for 0 min, the compact achieved only 94% density and did not show distortion. After sintering for 2 min, the compact achieved 98.9% density and started to distort. Distortion was significant after sintering for 5 min.

Discussion

In liquid phase sintering, densification and distortion are closely related to liquid content. With high liquid content full density can be achieved even at the particle rearrangement stage [1], but often is the concomitant distortion. With low liquid content the solid skeleton resists densification and also retain the compact shape. This was observed in our experiments. Low tungsten content samples achieved full density and distorted, while the 90W sample only achieved 94% density and did not distort.

Distortion in liquid phase sintering is also associated with low dihedral angles. In low dihedral angles, the reduction in solid-liquid surface energy on first melt formation leads to liquid penetration of grain boundaries [8]. Consequently, densification by rearrangement occurs rapidly and solid-solid bonds do not form before saturation of the intergrain void space [8]. Then the relatively weak capillary force is the only source of strength that disappears as the voids are filled with liquid. Distortion is the consequence

of strength loss, due to loss of solid skeleton strength or capillarity induced strength. Note that full density alloys will distort on reheating to liquid phase sintering temperature, demonstrating liquid attack of grain boundary. On the other hand, high liquid content alloys retain shape up to point of densification or pore closure.

Liquid penetration of grain boundaries leads to compact strength loss. A high solid solubility in the liquid correlates with a low dihedral angle and easy liquid penetration of grain boundaries. The fractional atomic solid solubility in the liquid can be approximately linked to the dihedral angle by the following empirical expression [8]:

$$k_A = 0.11 - 0.14 \frac{\phi}{2} \tan\left(\frac{\phi}{2}\right) \quad (1)$$

where k_A is the fractional atomic solid solubility in the liquid, and ϕ is the dihedral angle in radians. High solid solubility in the liquid k_A indicates a low dihedral angle according to Equation 1. The atomic solid solubility in liquid can also be linked to the dihedral angle by the following empirical equation [8]:

$$\phi = 75 - 638\Delta k_A \quad (2)$$

where Δk_A is the fractional atomic solid solubility change in newly formed liquid as compared with the solid solubility in the additive, and ϕ is the dihedral angle in radians. Equation 2 indicates that if the atomic solid solubility in liquid is much larger than the atomic solid solubility in the additive, the systems have low dihedral angles. In turn, low dihedral angles imply easier liquid penetration of the grain boundaries and often distortion.

Solid volume fraction and dihedral angle are the dominant factors controlling densification and distortion during liquid phase sintering [8]. A combination of high solid volume fraction and high dihedral angle results in slow densification without distortion. On the other hand, low solid volume fraction and low dihedral angle result in rapid densification with shape distortion. Such findings allow for mapping probable distortion and densification conditions versus material parameters of dihedral angle and solid content. The data and previous observations [5, 6, 8] with W-Ni-Cu, W-Ni-Fe, W-Ni, W-Cu, Mo-Cu, Mo-Ni, and Fe-Cu agree with the sinter map. We expect this map is also representative for other liquid phase sintering systems with spherical solid grains.

Strategies for Distortion Control in Liquid Phase Sintering

Various strategies emerge to improve distortion control in liquid phase sintering. Since the compact strength evolution determines densification and distortion onset, the design of compositions for densification without distortion requires manipulation of the microstructure and its evolution to sustain compact strength to avoid distortion. As compact strength has contributions from both sinter bonds and capillary forces, in principle, processing strategies that preserve sinter bonds and/or capillary forces will resist distortion. Liquid phase sintering systems that densify slowly resist distortion. These inherently have high solid volume fraction and high dihedral angle. So one option for distortion control is to use high solid volume fraction and high dihedral angle systems. Systems with low solid solubility in liquid inherently have a high dihedral angle and resist distortion. Compositions with presaturated liquid forming agents (for example, prealloy matrix) will inhibit dissolution of sinter bonds into liquid and resist distortion [8]. A slow heating rate at the point of liquid formation allows solid bonds to reform before capillary forces are lost with pore elimination and will resist distortion. Densification and distortion are sequential events during liquid phase sintering; the first focus is on densification. Densification occurs

first. Distortion is inhibited until after nearly full densification when capillary forces are lost and a solid skeleton is not formed. So sintering without full density will also resist distortion.

Conclusions

Solid volume fraction and dihedral angle are the dominant factors on densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and dihedral angle. On Earth, green porosity and pore size do not have observable effects on distortion in situation of fast densification where nearly full density is achieved or pores are closed and capillary forces are lost. Quenching results show that distortion is inhibited until pores are closed and the compact is nearly fully densified. Dimensional precision can be achieved by manipulating the microstructure and its evolution to sustain compact strength to avoid distortion in liquid phase sintering. Processing strategies emerge to improve distortion control in liquid phase sintering, including use of high solid volume fraction and high dihedral angle systems, low solid solubility in liquid, compositions with presaturated liquid forming agents, slow heating rate at liquid formation. Densification before full density or pore closure can also prevent distortion.

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USE OF COMPUTED TOMOGRAPHY FOR CHARACTERIZING MATERIALS GROWN TERRESTRIALLY AND IN MICROGRAVITY

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Computed Tomography (CT) has advanced considerably since being responsible for such dramatic advances in diagnostics within the medical field.¹ It has become a major tool in non destructive evaluation (NDE), and is used in many fields as diverse as coal-mining² to metal solidification³ to examination of rock cores.⁴ A review of industrial applications has been written by Dennis.⁵ It is only recently that the technique has been seriously used to determine composition through precise measurement of density.⁶ While such applications are restricted to cases when there is no ambiguity in the relationship of composition to density. Thus alloy solid solutions lend themselves to compositional analysis provided there is a large change in density with composition. The technique is most useful when rapid non-destructive evaluation is needed. Such cases will occur with samples returning from the International Space Station (ISS) when knowledge of the results could affect future strategies for processing of on-board samples. Experiments from those Principal Investigators (PI) that are most likely to benefit from early CT scanning are discussed. With a dearth of samples, the major emphasis in the first part of this project has been on preparing suitable standards, optimizing the CT technique for these applications, and using the CT system to determine density variations with temperature. An interesting application of CT has been in the examination of meteorites, which can be classified as space-grown materials and will certainly have solidified in a low gravity environment.

Theoretical Background to CT

The theory behind CT and particularly high energy CT (X-Ray) has been well described in the literature and will only be described briefly here. Fundamentally, a tomography system operates by measuring the intensity of a linear beam after attenuation by a volumetric sample. The sample (or samples) is moved and the attenuations collected from multitudinous directions. Mathematically, Radon⁷ discovered a method of transforming the many intensity readings into individual 2-dimensional absorption values. In specific cases these absorption values can be correlated directly to composition.

For adequate penetration of engineering samples, high energy beams such as X-Rays or gamma rays are necessary. The interaction of such beams with matter is shown schematically in Figure 1. Of specific interest is that within the Compton scattering regime, the absorption coefficient is directly proportional to the atomic number of the scattering center. This is not the case with the low energy region (dominated by photoelectric absorption), and in the high energy region (mainly pair production). The dominant interaction regions are shown as functions of mass attenuation coefficient (cm²/g) and atomic number with respect to photon energy are shown in Figure 2. Superimposed on this diagram is the energy of the ⁶⁰Co radioisotope which is the primary beam used in this work. ⁶⁰Co produces two energy levels of gamma rays, at 1.17 and 1.30 Mev. Of specific interest is that the absorption levels of these two energies is low enough that we can consider the system to be monochromatic.

Keywords: flight samples, composition, density, 3-D coarsening, meteorites, characterization

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Effectively, each incident beam of initial intensity I_0 , passing through the system is attenuated to the transmitted value I , with the attenuation being a function of the linear attenuation coefficient μ , and the thickness, s .

$$\text{Effectively} \quad I = I_0 \exp(-\mu s) \quad (1)$$

Along the entire path length, the attenuation is additive so that

$$I = I_0 \exp(-(\mu_1 s_1 + \mu_2 s_2 + \dots + \mu_n s_n)), \quad (2)$$

where μ_n is the linear absorption coefficient of the n th element in the path and s_n is its thickness.

In two dimensions and in terms of the active CT system, the position of the n th element can be described by coordinates x and y , so that the attenuation is

$$I = I_0 \exp[-\int_{\text{source}}^{\text{detector}} (\mu(x,y)) ds] \quad (3)$$

This equation becomes the Radon transformation of $\mu(x,y)$, the fundamental equation of the CT process

$$P = \ln (I_0/I) = \int_{\text{source}}^{\text{detector}} (\mu(x,y)) ds \quad (4)$$

The Radon transformation is shown in Figure 3. Basically these equations can be solved analytically from an infinite set of these integrals.

Practical Aspects of CT for Density Measurement

Effectively, the CT instrument measures a CT number for each x,y coordinate within a slice of a sample. Gray scale images can be obtained from the CT number to represent the absorption of the sample. This procedure is shown for a series of elemental standard materials of different, but known densities. Results produced by the ^{60}Co source as compared to an x-ray generator are shown in Figure 4. The darker the spot, the denser is the sample. The elements range in density from silicon and aluminum to lead and mercury. Some of the samples are porous, while others clearly show that an encasing fused silica tube is present. This figure also illustrates why the radioisotope is preferred for precise analytical work. The streaking evident in the x-ray image is the result of the continuous spectrum or Bremsstrahlung nature of the energy. The low energy x-rays are preferentially absorbed at the surfaces of samples so that the incident flux at the centers of the samples has a different energy spectrum from the edges. In this photograph, the streaks reflect that. In a quantitative analysis, the center would seem to be absorbing less than the surface, and an incorrect interpretation of absorption would result. The ^{60}Co source is effectively monoenergetic and avoids this problem.

The measurement of the CT number is also critical, as different values can be obtained by using different procedures. A distribution of CT numbers occurs across an entire two-dimensional section. Each absorbing element would have its own specific CT number so that a histogram is produced. In practice the sampling is limited to the region of interest which may include an encasing fused silica tube. Such a technique is shown in Figure 5. The histogram includes peaks for air, fused silica and copper. Selection of the appropriate CT number has been the subject of much investigation, particularly as the curve may not be centro-symmetric. Mode, peak position and several other mathematical functions have been tried, but the most important criterion is to use the same function for standards as for the sample being investigated.

The next step is to take the CT numbers for each sample and plot them against the density. The use of electron density (electrons per cubic Angstrom) can also be used for crystalline solids. Generally the calibration line thus produced has R^2 of 99%. A typical example is shown in Figure 6. While many of the standards are specifically made for the CT, in some cases problems arise because of porosity, which effectively reduces the density. In practice it was found that the use of end members as standards was the best solution for binary alloy systems.

Early Examples

The technique was first applied to determining compositional variations along ingots of mercury-cadmium telluride, a solid solution of cadmium telluride and mercury telluride, having a large density difference between the two end members. Macrocomposition values along a directionally solidified ingot are essential for determining the growth mechanism and the relative contributions of density driven convection and diffusion. In the past this has been done by the destructive and tedious technique of cutting and weighing the samples in air and in boiled (de-aerated) water. The CT technique proved superior without any loss of resolution. In figure 7, a sample grown at $0.1 \mu\text{m/s}$ is shown. This was to be the precursor for a sample to be flown on the fourth United States Microgravity Payload (USMP-4) flight mission, and required that the material be fabricated from several starting boules to obtain the initial desired composition profile. As cutting the sample into 2 mm slices to determine composition was undesirable, the CT method was applied to determine how best to fabricate the flight samples. Figures 8 and 9 respectively show the composition variation on the ground truth and flight samples, and also how the readings compare with electron microprobe analysis (wavelength dispersive) of the surfaces. There are definite differences in the readings. First of all, the CT will average the composition through a slice whereas the wavelength dispersive technique measures only the surface value. In the flight sample, problems with the translation device led to periodic fluctuations in the composition during the slow growth region (below 40 mm) which can be seen only with the microprobe. The quenched region (beyond 40 mm) also shows large fluctuations in the surface regions. Average readings as from the CT are essential for interpreting the growth process.

Candidates for CT Measurement from the Flight Program

As described above, the main requirement for composition determination via CT and density are that there be a measurable density difference between the constituent members. While originally intended for examining solid solutions such as mercury cadmium telluride, macrosegregation in directionally solidified eutectics and monotectics could also be revealed. The limitation is the spatial sensitivity of the technique. Candidates from the flight program are shown in Table 1. Fripp⁸, Lehoczky⁹ and Szofran¹⁰ are using solid solution materials, while Poirier¹¹ and Trivedi¹² will grow eutectic material with two phases. The table shows the densities and density differences between end members. For the eutectics, the presumed eutectic composition density and the end member (assuming a divorced eutectic structure) are given. While not in this table, the flight program of German (liquid phase sintering)¹³, Andrews (monotectic materials)¹⁴, and Stefanescu (particle behavior in composites)¹⁵ can also benefit from CT scanning. In past microgravity campaigns, both Andrews and Stefanescu used CT scanning for examination of their Sample Ampoule Cartridge Assemblies (SACA). Thermal expansion of the melt and the behavior of containing springs for the avoiding of bubbles were critical observations.

Ground-based results for germanium-silicon alloys are shown in Figures 10 and 11. Figure 10 shows a boule solidified after an alloy ingot of Ge-Si ingot was melted back onto a germanium seed, and then

directionally solidified. The build up of silicon during the initial transient can clearly be seen. In Figure 11 is shown a prospective single crystal to be used for growth initiation of an alloy crystal. While the photograph is a digital radiograph, and shows the presence of the germanium standard, the values quoted for the density are derived from CT scans at different locations within the seed crystal. Surface microprobe work could also obtain such readings, but an advantage of the CT is that an average value is obtained so that effects of radial segregation do not influence the results.

Density Measurements

CT has the advantage of being able to penetrate equipment in order to examine samples. Thus it is possible to measure the density of a sample within a furnace and hence determine density as a function of temperature. This can be done during and after the melting and back through a solidification cycle. The technique has the advantage of safety in that no exposed measurements need be made, and this also improves the overall thermal homogeneity of the system. Several elements have been examined at different temperatures using the CT system. Preliminary work was done on gallium and indium, but the main thrust has been on lead and a lead-antimony alloy.

A small single zone incorporating a heat pipe has been built specifically to be incorporated on the CT system. The furnace installed on the CT system is shown in Figure 12. The CT system at Kennedy Space Center (KSC) is referred to as second generation and the CT table translates through the incident beam, rotates a few degrees and repeats several times to acquire the desired number of views. While this operation disturbs the liquid, the effect, if anything, may be advantageous in reducing temperature gradients in molten samples. This would not be the ideal technique for examining liquid-solid interfaces during melting or solidification. The density can be measured by three different techniques. First, the length of the sample can be measured by making digital radiographs through the furnace. Secondly, the diameter of the sample can be measured while in the solid state, assuming the material has not melted against the container wall. Finally, the density of the material can be measured from the CT number, and converted to density. CT sections through the furnace and through standards are shown in Figure 13. Note that the furnace elements, the insulation, the heat pipe inner and outer walls and the heat pipe inner components all show up in addition to the lead sample and the standards. In other views, furnace thermocouples show up.

Digital radiographs of pure lead at increasing temperatures are shown in Figure 14. A plot of dilation with temperature derived from these data is shown in Figure 15. The data are influenced in the solid state by the presence of bubbles on the surface, and in the liquid state by the difficulty in reading the length as influenced by the meniscus. Nevertheless, the data are of credible quality. Figure 16 shows the density variation with temperature as measured by CT scans. The data are of excellent quality and compare with values in the literature, as can be seen from the accompanying data points.¹⁶ At present a sample of Pb-5.8% Sb is being evaluated and has been heated to 900°C, and is being measured by CT during the cooling. Further samples have been prepared including CdTe, and several compositions of HgCdTe. These latter have proved to be problematic at high temperatures due to the need to encapsulate them safely. The CT technique enables them to be evaluated safely and enclosed satisfactorily during the measurements.

CT of Metallic Meteorites

In the absence of man-generated long duration microgravity samples, two meteorites have been examined by CT to determine the inner structure. The objectives are to probe for compositional differences, particularly second phases, including compositional variations and, in coarse samples, any grain size

differences which could aid in the determination of age or cooling rate of the structure. Such an evaluation would normally be non-destructive. Such samples are normally unique and the maximum information has to be gathered without resorting to cutting and polishing. CT is proving to be useful.

The first sample was a privately owned sample of a meteorite which was found in China in the Nantan region. The sample was considerably corroded and was used as a test case to evaluate how well CT could demonstrate the inner structure. Following CT scanning of the entire piece, which was roughly 8 cm long and 4 cm diameter, a small section was cut from the center, polished, etched and examined by electron microprobe analysis. The oxidation proved to be considerable, and penetrated well into the sample. This is shown in Figure 17b, an oxygen map of the polished surface. Figure 17a is the CT scan through the same level and clearly shows the density difference evident between the iron-nickel alloy and the iron oxide. Clearly, the resolution of CT is inferior to the microprobe work, but with coarse grained samples, much information can nevertheless be obtained.

The second meteorite examined was from the Mundrabilla region of Australia. Discovered in 1916, two large slabs of 6 and 15 tons constitute the main mass. The smaller mass is shown in Figure 18a. The 6 ton slab has been cut into several 2 inch thick slices, which are on display in several museums throughout the world. The National Museum of Natural History (NMNH) in Washington houses one polished slice over 4 foot long and 2 foot across at its widest point. The structure displayed is very unusual in that it consists of primary iron-nickel grains with iron sulfide secondary phase in between them. The sample is extremely coarse, with the primary phase several cm across, and the sulfide phase, which constitutes some 25% by volume making up channels which are often broader than 1 cm. A slab was made available by NMNH which is 80 cm x 13cm x 15cm (Figure 18b). This is thicker than any of the slices, and proved to be within the limit of the ^{60}Co CT system. Small pieces were also made available for polishing. A typical microstructure is shown in Figure 19. The metallic phase is made up of the two common forms of the iron-nickel system found in meteorites, namely the high nickel face-centred cubic phase (taenite), and the low nickel body-centred cubic phase (kamacite). While not obvious in this sample the platelike structure of the kamacite phase (bottom right) has been produced by a eutectoid reaction and etching has revealed the famous Widmanstätten structure. The secondary sulfide is primarily troilite (FeS), but with thin parallel plates of daubreelite (FeCr_2S_4) present. Many other phases were present including a conical graphite phase, an example of which is “boxed” in Figure 18b.

Initially, 15 cm of the total length has been imaged at 1 mm intervals. The location of these scans is shown in the digital radiograph of Figure 20. Note that the sample is not removed from its containing wooden crate; the handles are clearly visible. Thirty five of the CT sections are shown in Figure 21, while a typical sample is shown in Figure 22. The density difference between the sulfide and the metal phase is clear. The graphite phase referred to above has a density between the metal and the sulfide. This is higher than anticipated due to the low spatial resolution and probable eutectoid-type mixing of the graphite and the metal. These 150 sections have been sequenced into an animation, and are being prepared for 3-D visualization. While many of the microscopically visible features are not seen in the CT scans, the animation demonstrates the nature of the distribution of the sulfide with respect to the metal, the exact conical nature of the graphite and the presence of other low density rounded features within the metal. These have not yet been identified. The entire length of the sample will be finally examined.

Conclusions

The CT technique has demonstrated the ability to perform high quality chemical composition analysis on solid solutions, and the potential for evaluating flight samples within their ampoules has also proved possible. It has been shown that in situ measurements of dilation and density are possible using a furnace installed on the CT system. Finally, the CT technique has been useful for evaluating the internal structures of two component meteorites.

Acknowledgements

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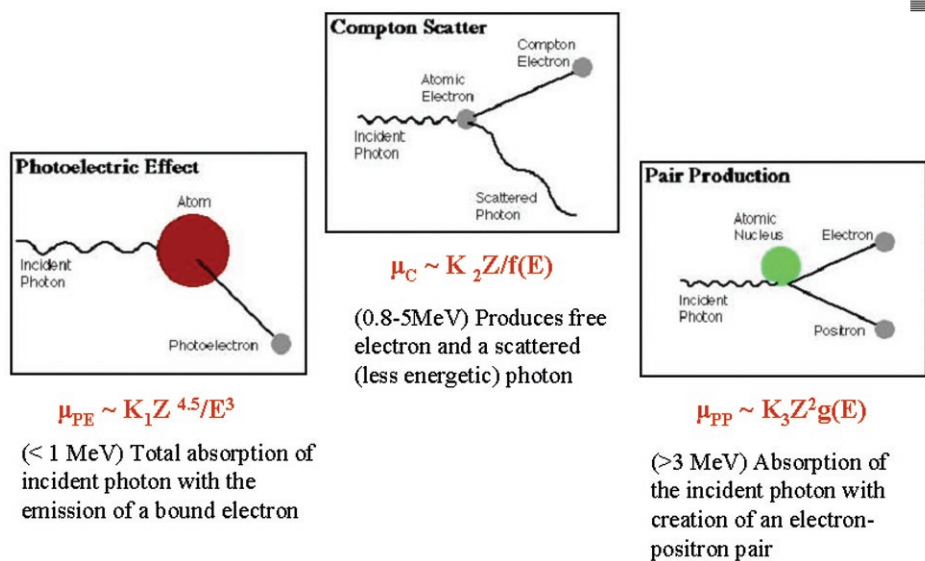


Figure 1. Photon Scattering Mechanisms

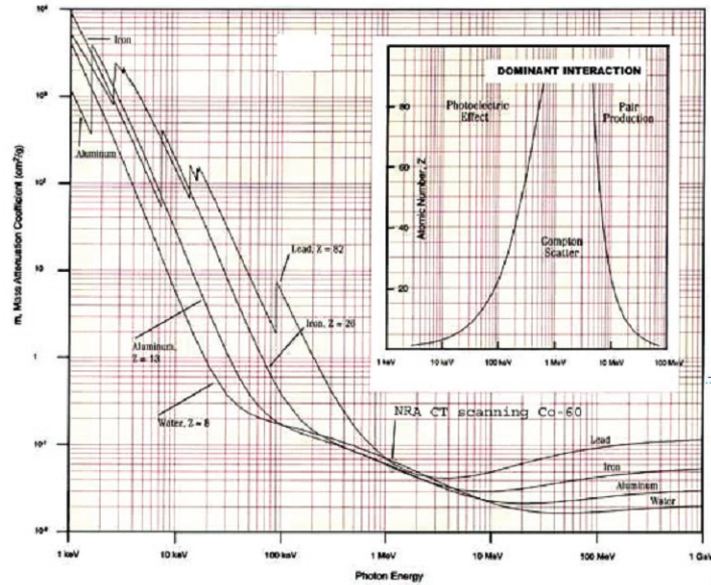


Figure 2. Energy Dependence of Attenuation

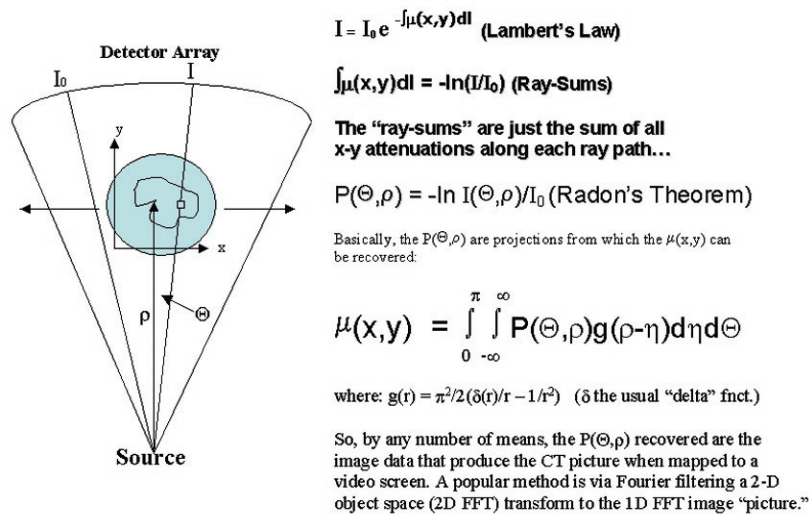


Figure 3. Fundamentals of the Radon Transformation

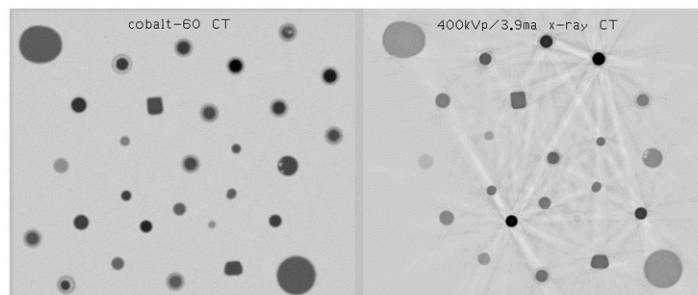


Figure 4. CT scans of an array of standards with gamma(left) and X-Rays (right)

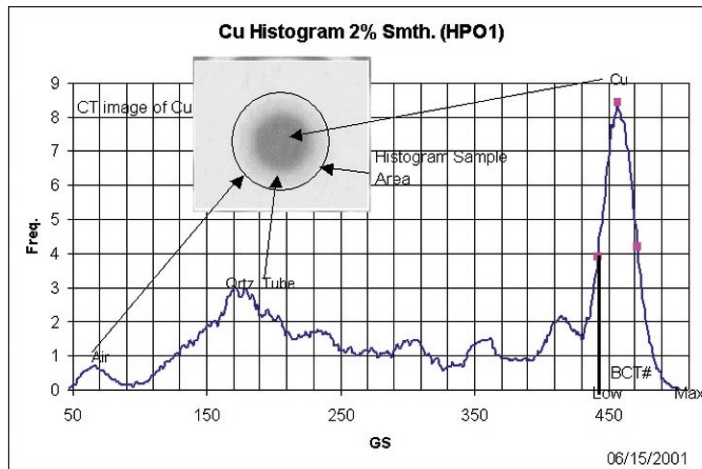


Figure 5. Histogram of Cu standard within a fused silica tube

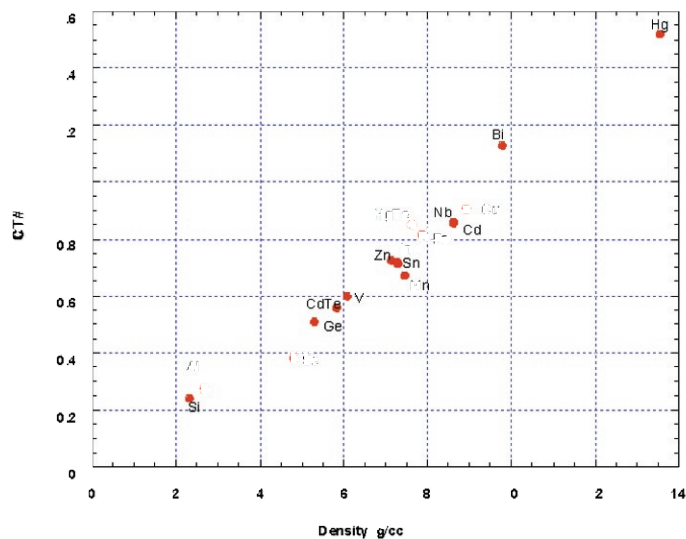


Figure 6 Typical Standard Set for Quantitative Density Measurement

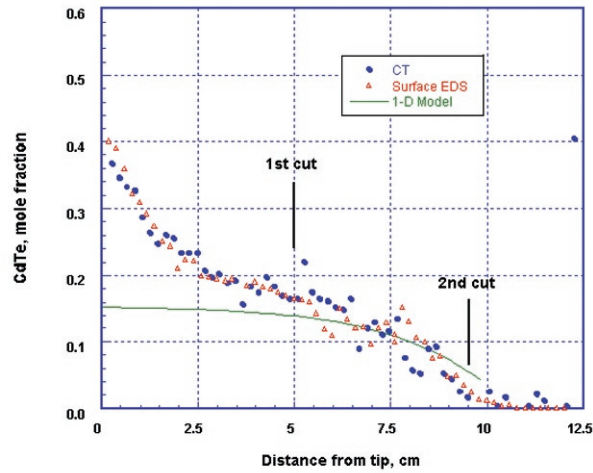


Figure 7. CT determined composition data for a directionally solidified mercury cadmium telluride solid solution

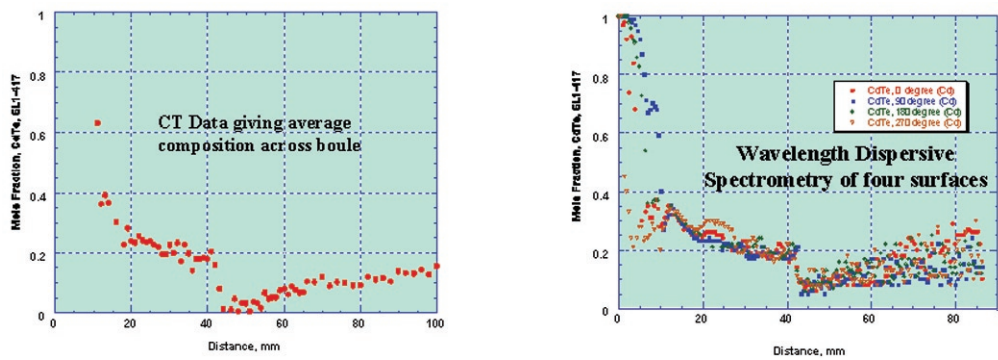


Figure 8. A Comparison of CT (left) and Wavelength Dispersive Spectrometry (WDS) of four surfaces on a ground-grown crystal of HgCdTe

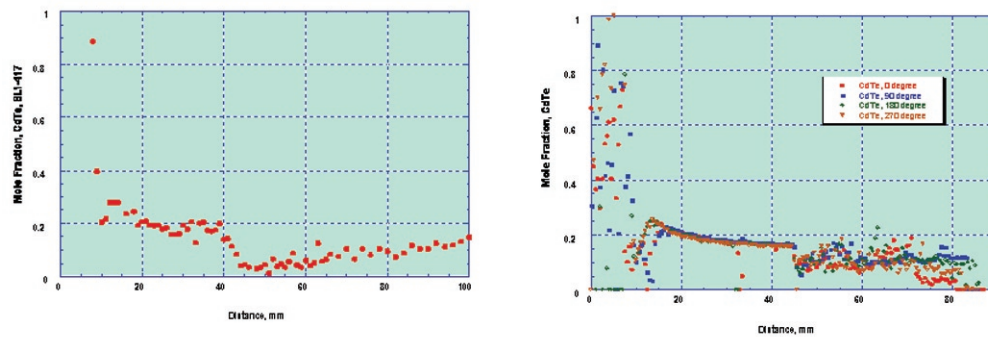


Figure 9 . A Comparison of CT (left) and Wavelength Dispersive Spectrometry (WDS) of four surfaces on a microgravity-grown crystal of HgCdTe

Material	Alloy 1	Alloy 2	Δ Density	PI
PbSnTe	PbTe 8.27 g/cc	SnTe 6.53 g/cc	26%	Fripp
HgCdTe	HgTe 8.112	CdTe 5.852	38%	Lehoczky
GeSi	Ge 5.325	Si 2.329	129%	Szofran
Pb-Sb	Pb 11.341	Pb/.058Sb 11.071 Pb/.135Sb 10.74 Sb 6.697	2.4% 5.3% 40.9%	Poirier
Al-Cu	Al 2.699	Al/.04Cu 2.948 Al/.33Cu 4.78 Al/.54Cu 7.06	9.2% 77% 162%	Trivedi

Table 1. Candidate Materials for Quantitative CT Scanning

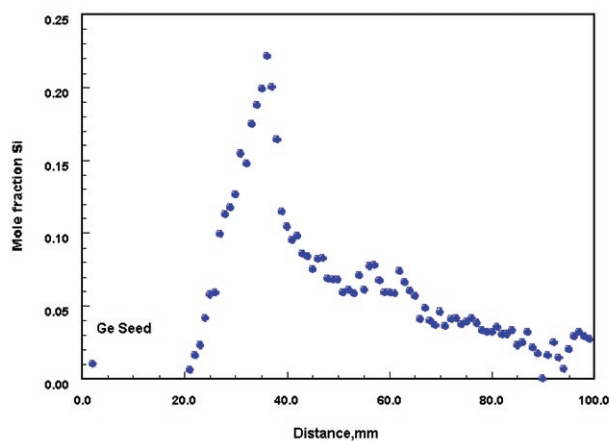


Figure 10. CT of an alloy crystal of germanium-silicon seeded from germanium

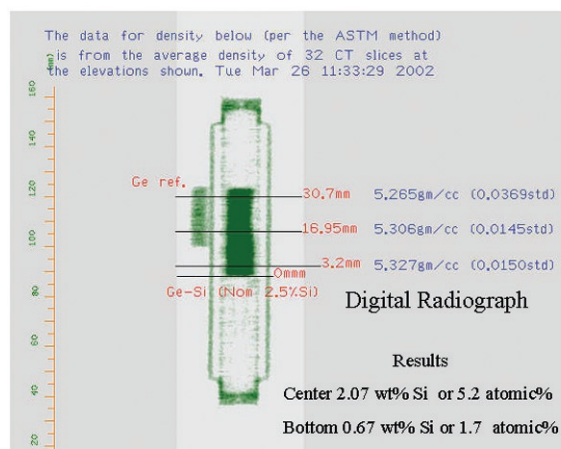


Figure 11. Digital radiograph of a germanium-silicon alloy seed crystal

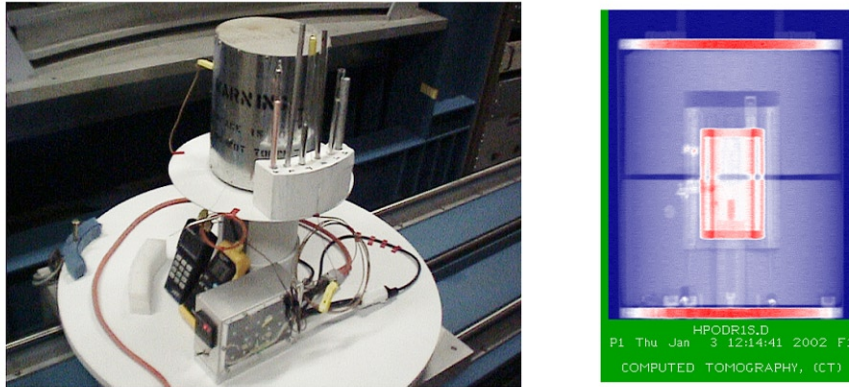


Figure 12. MSFC-designed and built furnace residing on the CT translation stage at KSC (left), and digital radiograph of the furnace (right). Note the elemental standards outside the furnace

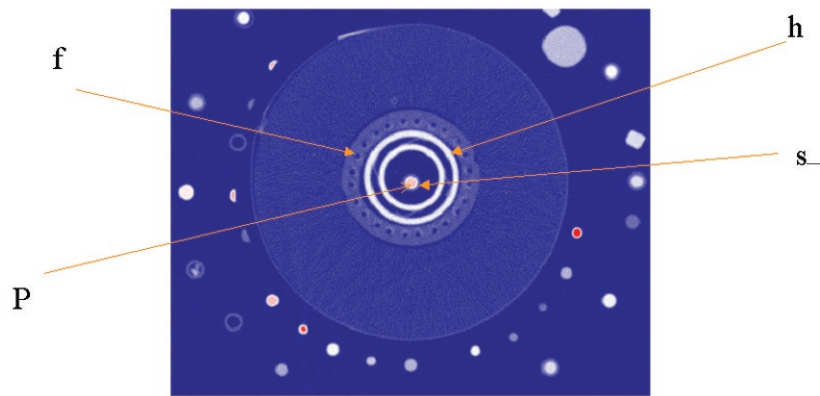


Figure 13. CT section through furnace and lead sample (p). Furnace windings (f), heat pipe (h), and fused silica tube (s) all show clearly

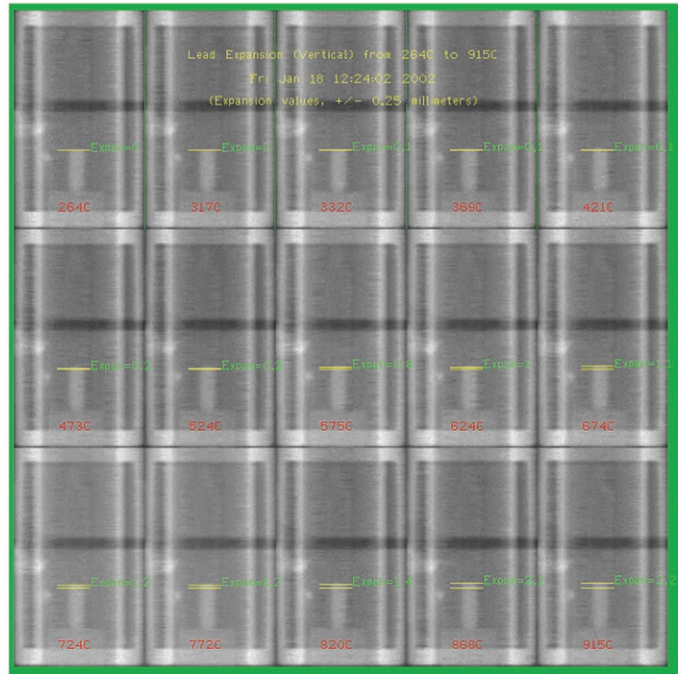


Figure 14. Digital Radiographs showing thermal expansion of Lead

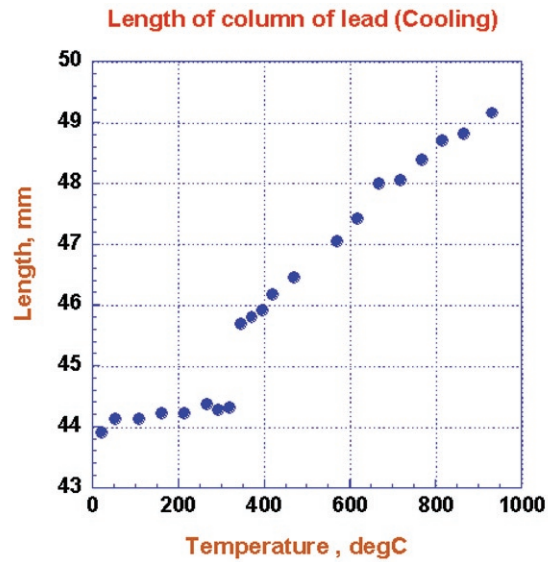


Figure 15. Dilation of lead on cooling from 900°C to room temperature

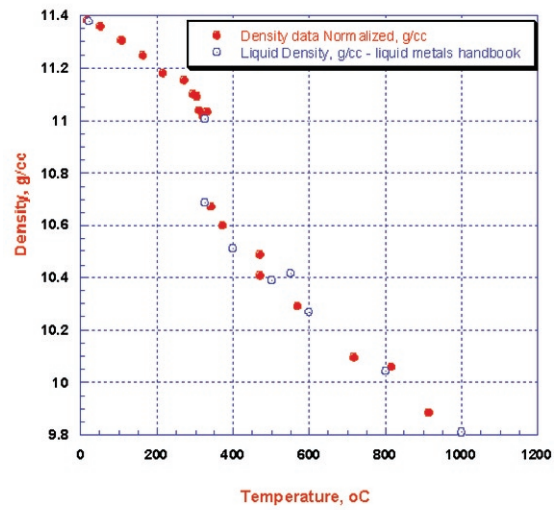


Figure 16. Density of Lead as determined from CT Data

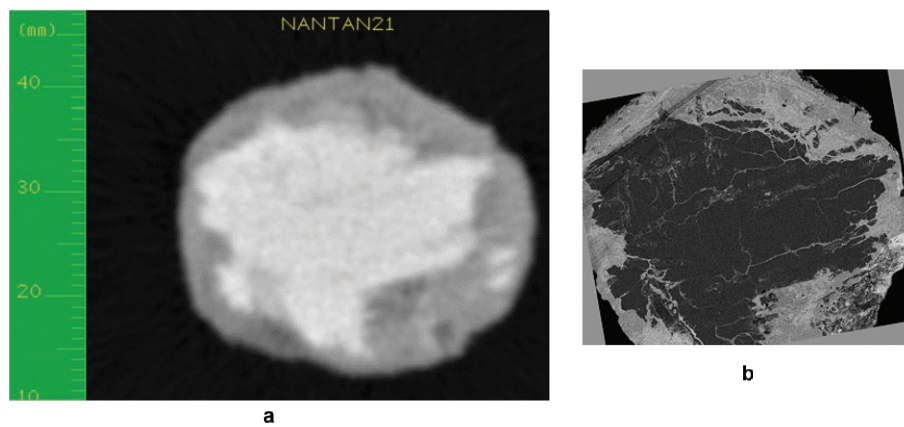


Figure 17 Image of structure of Nantan meteorite from CT (left) and after cutting and polishing (right). The polished surface shows an oxygen image determined using electron microprobe (light color means higher concentration)



a



b

Figure 18. The Mundrabilla meteorite. 6 ton piece as found (upper), and part of the 80 cm slab as polished at MSFC (lower). Note the fanshaped graphite (outlined)



Figure 19 Macro photograph of the structure of the Mundrabilla meteorite. The iron-nickel Widmanstätten structure is demonstrated by the grain on the bottom right, while the striated sulfide structure is the troilite with parallel daubreelite inclusions.

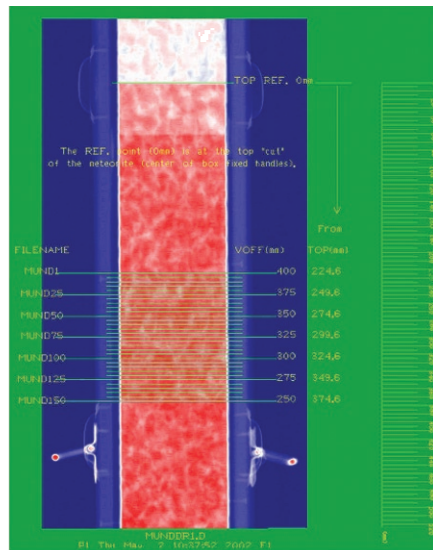


Figure 20. A Digital Radiograph of the Mundrabi a meteorite demonstrating the region subjected to the first series of CT scans.

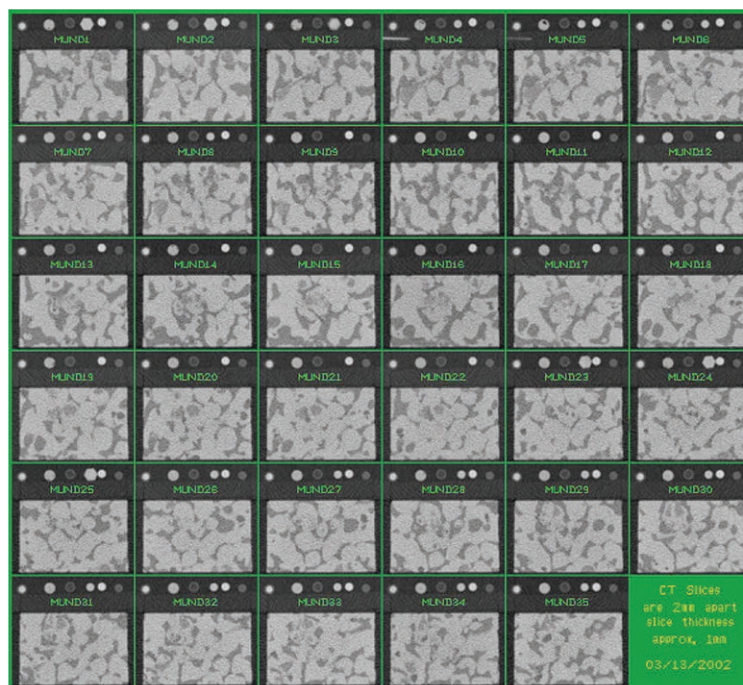


Figure 21. Thirty six of the first 150 CT scans made on the Mundrabi a meteorite

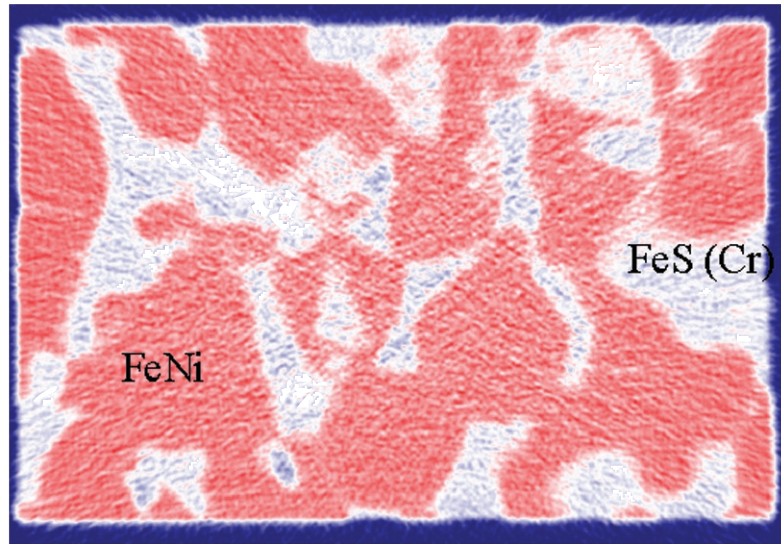


Figure 22. A color enhanced CT scan showing the metallic phase (dark red) and the sulfide phase (light, blue)

RIDGE/IDGE A SUCCESSFUL DENDRITIC GROWTH EXPERIMENT

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Dendrites (tree-like crystals) represent highly evolved microstructures arising from unstable solid-melt interfaces. In fact, dendrites are the ubiquitous form of crystal growth encountered whenever metals and alloys solidify freely from supercooled melts, or solidify directionally under low thermal gradients. The Isothermal Dendritic Growth Experiment, or IDGE, is a basic science experiment designed to provide terrestrial and microgravity data that measure the kinetics and morphology of dendritic solidification under pure heat conduction control. The IDGE flew three times as a primary payload on the USMP-2, -3, and -4 missions, in 1994, 1996, and 1997, respectively, aboard the US Space Shuttle *Columbia*. These flight experiments provided the first solid evidence that Ivantsov's heat conduction solution closely describes dendritic growth for the test materials succinonitrile (SCN) and pivalic acid (PVA). These organic crystals, offer three major experimental advantages compared to metals: they are transparent, easily purified to high levels, and have conveniently low melting points. The on-board IDGE instruments provided CCD images (telemetered to Earth during the flights), NASA-processed 35-mm film negatives (available postflight), and for the first time on USMP-4, near-real-time streaming of video data telemetered to our laboratory via the K-band (high-frequency) antenna on the shuttle. IDGE data in its totality, as reported elsewhere, consisted of hundreds of repeated experiments on steady-state dendritic growth. These data provide benchmark quality crystal growth speed as well as tip radii measured as functions of the melt supercooling, ΔT . The RIDGE program is designed as a follow-on to an ongoing MRD flight program, to frame the case that continuing ground-based data reduction and analysis will greatly enhance the understanding of existing or potential flight experiments in materials science.

Introduction

Two major subjects constituted the RIDGE focus over the past year: PVA sidebranching characteristics, and PVA dendrites melting in microgravity environment. The sidebranch characteristics of pivalic acid dendrites grown under convection-free (cf) and diffuso-convective (dc) conditions were investigated for supercoolings over the range of 0.1K to 1.0K. Results indicate that the distance from the dendrite tip to the first detectable sidebranch and to the first detectable coarsening event normalized by the tip radius, R , are independent of the supercooling. The sidebranch spacing in the uniform region near the dendrite tip, and the spacing in the coarsening region when normalized by R , do not appear to have a significant dependence on convection or supercooling. When the envelope enclosing all sidebranches from the tip to the end of the coarsening region was fitted to a power law as a function of distance from the tip, we found that the pre-exponential and exponential terms were significantly different for the convection-free and diffuso-convective results. This supports the observation that the absence of convection seems to alter the size of the sidebranches. Lastly, the predictions from theoretical models of sidebranch spacings are much

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lower than experimental observations, while the predicted sidebranch amplitudes were larger than those observed.

Steady-state crystal growth data from the IDGE, documented elsewhere, indicate that dendritic growth under microgravity conditions is limited by conduction heat transport. We now report on the melting process of a PVA dendritic mushy zone, observed for the first time under convection-free conditions. Conduction-limited melting processes are of importance in orbital melting of materials, meteoritic genesis, mushy-zone evolution, and in fusion weld pools where the length scales for thermal buoyancy are highly restricted. Microgravity video data show that PVA dendrites melt into fragments that shrink at accelerating rates to extinction. The melting paths of individual fragments follow a characteristic time dependence for the diminishing length scales within the mushy zone. The theoretical melting kinetics against which the experimental observations are compared is based on the conduction-limited quasi-static process of melting under shape-preserving conditions. Good agreement between quasi-static developed theory and experiment was found for the melting of a needle-shaped prolate spheroidal PVA crystal.

A. Sidebranch Study

A.1 First Detectable Sidebranch

The first detectable side branch was defined as the first protrusion from the dendrite which produced a detectable and measurable peak in the intensity curve. These coordinate values were normalized using the tip radius, averaged, and the standard deviation found. There was no apparent variation of the normalized distance to the first detectable sidebranch with supercooling, within the range of standard deviation, for the diffuso-convective or convection-free data (Figure 1). Hence, this relationship can be represented as a linear scaling law,

$$D_o = C_o R \quad (1)$$

where D_o is the distance to the first detectable sidebranch, R is the measured dendrite tip radius and C_o is the scaling constant. Based on analysis of the data in Figure 1, the value of the scaling constant in convection-free conditions is $C_{o(cf)} = 33.6 \pm 4.9$ and in diffuso-convective conditions, $C_{o(dc)} = 29.6 \pm 3.1$.

To determine if the diffuso-convective and convection-free results are statistically significantly different, a two-tailed student t-test was performed on the results with a 95% confidence level. It was assumed the data came from a Gaussian-shaped population and had unequal population variances, due to a significant difference in the average variance between the data sets. The t-test examines two data sets (with their attending statistical averages) and determines the likelihood that two data sets come from the same population. That is, the t-test is used here to help determine whether differences in the average values are *meaningful*, or due to the natural stochastic character of dendrite sidebranches. The two-tailed test was used because it is unknown which direction any variation between the data sets could occur. If the t-test produces a probability of less than 5% it signifies that the averages of the data sets are significantly different, and the differences can therefore be attributed to the difference(s) in test conditions with a 95% confidence level. Comparison of the normalized distance to the first detectable sidebranch using the t-test, produced a probability of 0.024 which signifies that there is a statistical difference between the averages of the convection-free and diffuso-convective data sets. We do not know whether such a difference is due to a fundamental issue in dendritic sidebranching, or is perhaps due to other differences between the data sets such as the different convective conditions, or the fact that the data sets compared are not are not perfectly matched supercooling per supercooling.

A.2 First detectable coarsening

The first detectable coarsening is defined here as the first sidebranch, for which when moving away from the tip, the amplitude is less than for the previous sidebranch. The distance to the first detectable sidebranch in the coarsening region was measured and the normalized average and uncertainty calculated. It appears that there is no variation, within the range of standard deviation, of the normalized distance to the first coarsening as a function of the supercooling (Figure 2). Hence this relationship can be represented as

$$D_c = C_c R, \quad (2)$$

where D_c is the distance to the first coarsening, and C_c is the scaling constant. Based on Figure 2, $C_{c(cf)} = 70.4 \pm 10.8$ for convection-free conditions and $C_{c(dc)} = 60.2 \pm 8.3$ for diffuso-convective conditions. The t-test with 95% confidence between the data sets yielded a probability of 0.001, which indicates there is a difference between the convection-free and diffuso-convection data sets. Again, we make no claim to the source of this difference.

A.3 Sidebranch spacing in uniform region

The difference in the x positions of two adjacent sidebranches is defined as the sidebranch spacing. As reported above, the first coarsening occurs at a distance of approximately 60-71 radii behind the tip. Hence to ensure the uniform region does not contain a coarsening event and is consistent for each growth, it has been defined here as the region between the first detectable sidebranch and a distance equal to 55 radii behind the tip.

The sidebranch spacing was measured in the uniform region, normalized with respect to the radii, and the average and standard deviation calculated. From Figure 3, it appears there is no variation, within the range of standard deviation, of the normalized value of the sidebranch spacing in the uniform region as a function of the supercooling. Hence this can be represented as

$$C_u = C_u R, \quad (3)$$

where C_u is the sidebranch spacing in the uniform region, and C_u is the scaling constant. Based on Figure 3, the scaling constant under convection-free conditions is $C_{u(cf)} = 5.01 \pm 0.84$ and $C_{u(dc)} = 4.56 \pm 0.64$ for diffuso-convective conditions. A two tailed t-test performed on the data produced a probability of 0.0534 which indicates that there is not a statistical difference between the results within a 95% confidence level. This lack of a statistical difference is especially noteworthy since, as noted previously, the two data sets are not perfectly identical in their experimental conditions.

A.4 Sidebranch spacing in the coarsening region

The sidebranch spacing in the region further behind the tip where coarsening occurs was measured. The coarsening region was defined as beginning at a distance of 55 radii behind the tip and ending at 200 radii to maximize the number of sidebranches and maintain consistency between growths.

The spacing for each growth was normalized, averaged and the standard deviation calculated. It appears that there is no variation, within the range of standard deviation, of the normalized value of the sidebranch spacing in the coarsening region as a function of supercooling (Figure 4). Hence this can be represented as

$$\bar{e}_{cr} = C_{cr} R, \quad (4)$$

where C_{cr} is the sidebranch spacing in the uniform region, and C_{cr} is the scaling constant. Based on Figure 4, the scaling constants are $C_{cr(cf)} = 6.98 \pm 1.18$ and $C_{cr(dc)} = 6.55 \pm 0.96$. A two tailed t-test performed on these results (probability = 0.1945) indicates there is no statistical difference between the results due to convection forces within a 95% confidence level.

A.5 Sidebranch envelope

To characterize the shape of the sidebranch envelope, the position of the sidebranch tips from the dendrite tip (x coordinate) were linearly regressed in the power law form shown in Equation 10, where the y coordinate is the coordinate normal to the growth axis, or the amplitude of the branches. α is the pre-exponential term, and β is the exponential term.

$$\frac{y}{R} = \alpha \left(\frac{x}{R} \right)^\beta \quad (5)$$

The values of α and β were averaged for each growth and plotted versus supercooling as shown in Figures 5 and 6. It appears that these values are independent of supercooling. Writing these values in the form of Equation 10:

$$\left(\frac{y}{R} \right)_{cf} = (0.87 \pm 0.26) \left(\frac{x}{R} \right)^{(0.73 \pm 0.09)} \quad (6)$$

and

$$\left(\frac{y}{R} \right)_{dc} = (0.65 \pm 0.19) \left(\frac{x}{R} \right)^{(0.82 \pm 0.09)} \quad (7)$$

The t-test indicated the convection-free and diffuso-convective environments produced significantly different α and β values (probability of 0.0036 for α and 0.00068 for β). These differences are clear based on the uncertainty measurements alone with out reference to the student t-test.

B. Melting in Microgravity

Specifically, we analyzed and reported the first on-orbit video data that record carefully-controlled growth and melting sequences in convection-free dendritic mushy zones obtained under microgravity conditions (Figure 7). This paper provides an analysis of melting sequences of already formed dendrites in microgravity—a subject not developed in much detail in the prior literature.

B.1 Mushy Zones

Dendrites are the key microstructural components of mushy zones. A mushy zone is defined as a finely-mixed two-phase region, consisting of a dendritic primary solid phase embedded within its melt phase. Mushy zones are known to be present in ingots, castings, and welds, and thought to play a role in the evolution of the Earth's core, and planetesimals. The mushy zone represents the “active” region in a solidifying body in which the microstructure forms and evolves. The dendritic structures that form in mushy zones are often highly ramified, as a result of the growth of multiple primary dendrites and the subsequent development of secondary, tertiary, and even higher-order side branches. Consequently the length scales for melt convection within mushy zones are usually small, micron-sized pockets of melt remaining between dendrite arms. Under terrestrial conditions, to characterize a mushy zone one must understand a number of complex processes. These include conduction and convection of latent heat, solid-state diffusion of solute segregated among the dendritic branches, limited convective transport of solute

in the melt, and capillary effects such as remelting and phase coarsening. In order to simplify the behavior of a melting mushy zone, we studied pure PVA (4-9's purity) under nearly gravity-free conditions. In a carefully controlled microgravity environment $g \leq 10^{-6}g_0$ where g_0 has the terrestrial value of 9.8 m/s^2 the melting of a mushy zone in a pure substance should be kinetically controlled by a conduction-limited heat transfer process, perhaps slightly modified by capillarity.

B.2 Analysis of IDGE video data

The freezing and melting data analyzed and reported here are near-real-time 30 fps video downlinked from the third and final IDGE microgravity experiments. The IDGE video database represents a unique compilation of scientific information concerning the kinetics of freezing/melting of PVA (FCC) dendritic crystals. On-board video signals generated within the IDGE were downlinked via the Shuttle's K-band antenna, and recorded by NASA on 8mm tapes using a high-resolution VTR. The analog data were transferred via coaxial cable to an image capture card using commercial software (VideoSavant®). Two hours of 30fps, 640x480 pixels, 255 gray-scale images are captured on a single, large image buffer file, accessed by VideoSavant®. The image processor/compiler required approximately 70 Gb of hard drive memory. Once the image buffer is viewed by software, we could export the digitized video at the desired rate in the following file types: .avi-files for illustration, .tiff-files or .jpeg-files for analysis.

For each freezing/melting cycle, the video data (steps 4 and 5) were exported as individual .tiff files for every tenth frame. For the last minute of melting, toward the end of step 5, where the thermal fields approach the stable melt temperature, approximately 1.8K above T_m , individual .tiff files were exported for every video frame.

As melting begins, the tertiary dendritic side-arms begin to shorten, and the larger secondary branches detach from the primary stem. Figure 7 shows several stages of the melting sequence. In microgravity the individual crystalline elements of the mushy zone remain completely motionless. We did not observe any sedimentation of the fragments of denser solid. At the final stages, the remaining dendritic fragments present a large variety of shapes, from nearly spherical blobs to elongated needle-like crystals, all of which eventually melt away.

The mushy-zone melting events recorded every $1/30$ th second as digital frames provides, to our knowledge, the first data compilation of convection-free melting over a significant range of length scales, from about 10^{-2}m down to about $5 \times 10^{-5}\text{m}$. The large dynamic range of these length scales allows a detailed kinetic analysis of the convection-free melting process.

B.3 Image Processing

The shapes of the melting dendritic fragments, as analyzed from the IDGE video data, were determined using commercial image analysis software (ImagePro®4.0). The fragments, particularly toward the later stages of melting, are best described as prolate spheroidal particles. The equivalent ellipse of the two-dimensional image of this fragment is calculated on the basis of its major axis, C , and minor axis, A . The physical particles are, of course, three-dimensional objects, approximated as prolate spheroids of decreasing size. A prolate spheroid is an ellipsoid where the two minor axes are equal. Image analysis permitted measurement of the major and minor axes of the equivalent ellipsoidal fragment as a function of time. Sampling the C/A ratio over time towards the end of the melting cycle shows that the values of the C/A ratio for a particular fragment do not vary much. Figure 8 shows how the C/A ratio changes with

time. For the particular crystal measured the C/A ratio varies from a starting value of about 11, rises to a maximum of about 14, and decreases to a value of 10 with about 95% of the crystal's volume melted. Thus, the C/A ratio for the melting fragment may be approximated by its volume-weighted average, which in this instance is $C/A = 12.0$.

Quasi-static and moving boundary solutions are well known for the growth of spherical crystals for which $C/A = 1$. For the more general cases of ellipsoids and hyperboloids, moving boundary solutions were developed by Ham. However, Ham's similarity solutions for ellipsoids apply only to the case of crystal growth. Ham clearly states in his paper that the similarity transformations used in his moving boundary solutions are inapplicable to cases of ellipsoidal particle melting. Lacking an analytical moving boundary solution, we developed a quasi-static model for the conduction melting of prolate spheroids, and subsequently demonstrate that the melting kinetics, without convection, of needle-like dendritic fragments is accurately described as a conduction-limited process.

B.4 Results

The crystal analyzed in microgravity formed originally as a part of a dendritic mushy zone in the IDGE growth cycle 4. The dendrites grew from pure molten PVA supercooled 0.4K. The mushy zone consisted of approximately 4 % dendritic solid when melting was initiated. The time to melt this mushy zone completely was approximately 12 minutes. The last fragment to melt was the one selected for analysis. (See again the last panel of Figure 7.) This dendrite fragment ($C_0 = 0.76\text{cm}$) was the residual crystal from the melting primary dendrite stem, and exhibited a nearly constant aspect ratio $C/A \approx 12$ throughout its final 40s melting sequence. To calculate the melting kinetics of this dendritic fragment, one must know, in addition to the C/A ratio, the thermal diffusivity and the Stefan number of the melt. The thermistors arranged within the IDGE thermostat were optimized for measuring the supercooling prior to dendritic growth quite precisely ($\pm 0.002\text{K}$). Unfortunately, the subsequent temperature history within the growth chamber, especially during the melting portion of an experimental growth cycle, is less certain. In view of this situation, one may adopt a self-consistent method of estimating the Stefan number in the melt during the last 40s of the video melting sequence. The basis of the value of the self-consistent Stefan number is the observed extinction time of the fragment, $t^\dagger$. The extinction time (in this instance, 40s) is the interval needed for the melting crystal to disappear. The extinction time can be measured precisely to within 1 videoframe ($\pm 0.033\text{s}$), and the thermal diffusivity of molten PVA at its melting point is known to be $\alpha_l = 7.0 \times 10^{-4} \text{ cm}^2/\text{s}$. Inserting these values and $K_{\text{prol}} = 360.6$ yields the self-consistent Stefan number based on extinction time of $St^\dagger = 0.057$. The crystal melting data reported were fit in their entirety using this self-consistent Stefan number, which corresponds to the melt being superheated 0.63K above its equilibrium melting point, $T_m = 35.97\text{K}$. Scrutiny of the data points shows that there are slight disparities over the melting interval. Particularly as the extinction time is approached, some capillary effects may enter the kinetics and speed up the melting beyond that calculated by quasi-static theory. These are clearly minor effects, and they will be explored in future studies.

Possible melting behaviors for prolate spheroidal crystals with C/A ratio subjected to different Stefan numbers are shown for comparison in Figure 8. These curves are predicted using a quasi-static approach and the indicated Stefan numbers, which were selected to cover the range of values encountered during the entire melting portion of the experimental cycle. Note that the melting kinetic curves for $C/A = 12$ change substantially with only modest variations in the Stefan number.

Conclusions

A.1. The sidebranch characteristics of pivalic acid (PVA) dendrites grown under convection-free and diffuso-convective conditions were investigated as a part of the Isothermal Dendritic Growth Experiment (IDGE). We compared convection-free and diffuso-convective results for PVA to both the results for succinonitrile (SCN) and with theoretical models of dendritic side branching.

2. These comparisons indicate that the distance from the dendrite tip to the first detectable sidebranch and to the first detectable coarsening normalized by the tip radius appear to be independent of supercooling, but may be slightly affected by convection. In convection-free conditions the normalized distance to the first sidebranch and first coarsening event occur further from the tip than under diffuso-convective conditions. This could be due to the change in convection conditions and the local thermal gradient near the sidebranches, which may alter the rate of sidebranch growth. The dependence on convection was not observed in previous work conducted on SCN [20].

3. Normalized sidebranch spacing in the uniform region and the coarsening region do not appear to have significant dependences on supercooling or convection. The sidebranch envelope could be fitted to a power law equation, where the pre-exponential and exponential terms calculated were found to be significantly different for the convection-free and diffuso-convective results. Convection also appeared to affect the sidebranch envelope in SCN dendrites [20]. These results seem to indicate convection affects the thermal conditions near the solid-liquid interface, which alters the amplitude rather than the spacing of the sidebranches.

B.1. Dendritic mushy zones were formed in supercooled high-purity PVA melts in microgravity on the third IDGE space flight experiment. At the end of each experimental cycle the mushy zone was progressively melted by raising the temperature of the thermostat. Video data at 30 fps of the melting process for one cycle (0.4K supercooling) are reported here. Upon raising the temperature, the mushy zone melts into numerous fragments, many of which may be characterized as prolate spheroids.

2. Individual dendritic fragments remain motionless in the low-gravity environment, progressively melting toward extinction at nearly constant C/A ratios.

3. Moving boundary solutions, such as those proposed by Ham for ellipsoidal crystals, are not applicable to melting processes. In lieu of a numerical solution to the moving boundary problem, we developed a quasi-static analytic theory, using curvilinear coordinates. The theory describes the kinetics of conduction melting of prolate spheroids of arbitrary C/A ratios. The quasi-static analytic results are limited to small Stefan numbers.

4. The observed melting kinetics in microgravity of a prolate spheroidal crystal with an aspect ratio $C/A=12$ was found to be described accurately by the quasi-static analysis. Predictions of the crystal size as a function of time require knowledge of the Stefan number, the melt's thermal diffusivity, and a kinetic parameter derived from the theory that accounts for the crystal's aspect ratio.

5. The Stefan number for this work was found from the extinction time of the crystal. Temperature data telemetered directly from the orbiting IDGE thermostat yield a Stefan number in good agreement with the

value derived from the extinction time of the prolate spheroid analyzed. The predicted convection-free melting kinetics accurately describe the experimental observations in microgravity.

6. Future work will be directed at obtaining a direct precision measurement of the Stefan numbers using in situ thermometry, and exploring the influences of the initial supercooling that affects mushy zone morphology and density. In addition, small disparities discovered between the microgravity melting data and quasi-static theory, perhaps caused by ignoring capillary effects, will be the subject of future enquiry.

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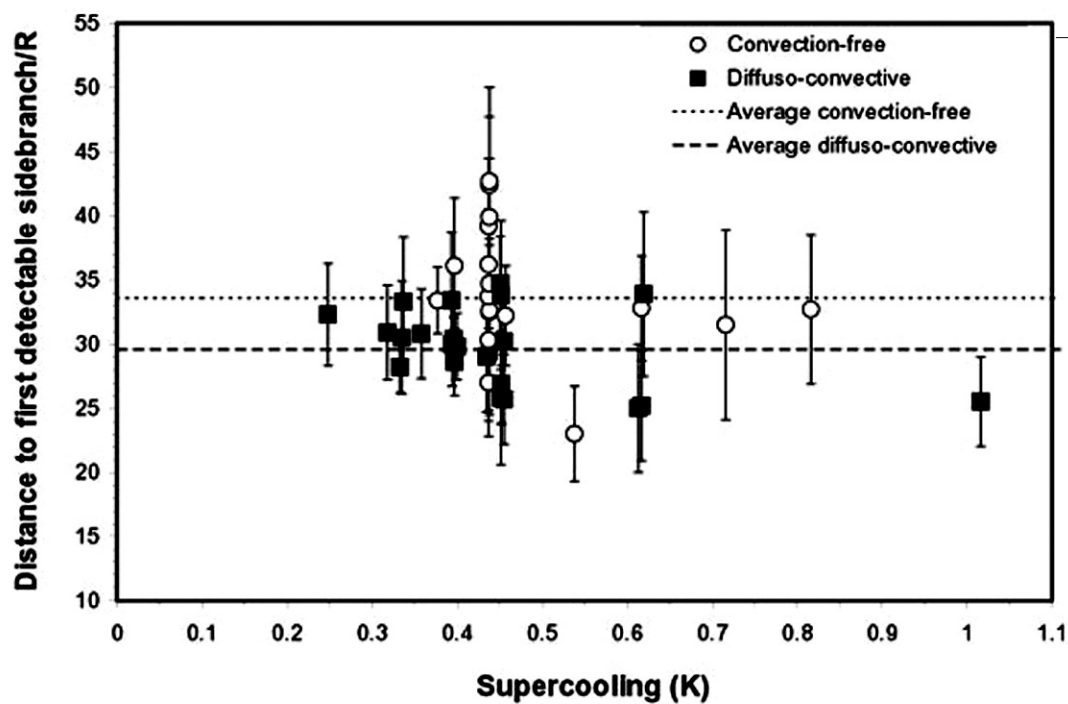


Figure 1: Distance to the first detectable sidebranch normalized by the tip radius as a function of supercooling for convection-free and diffuso-convective data. There is significant statistical difference between the convection and convection-free averages.

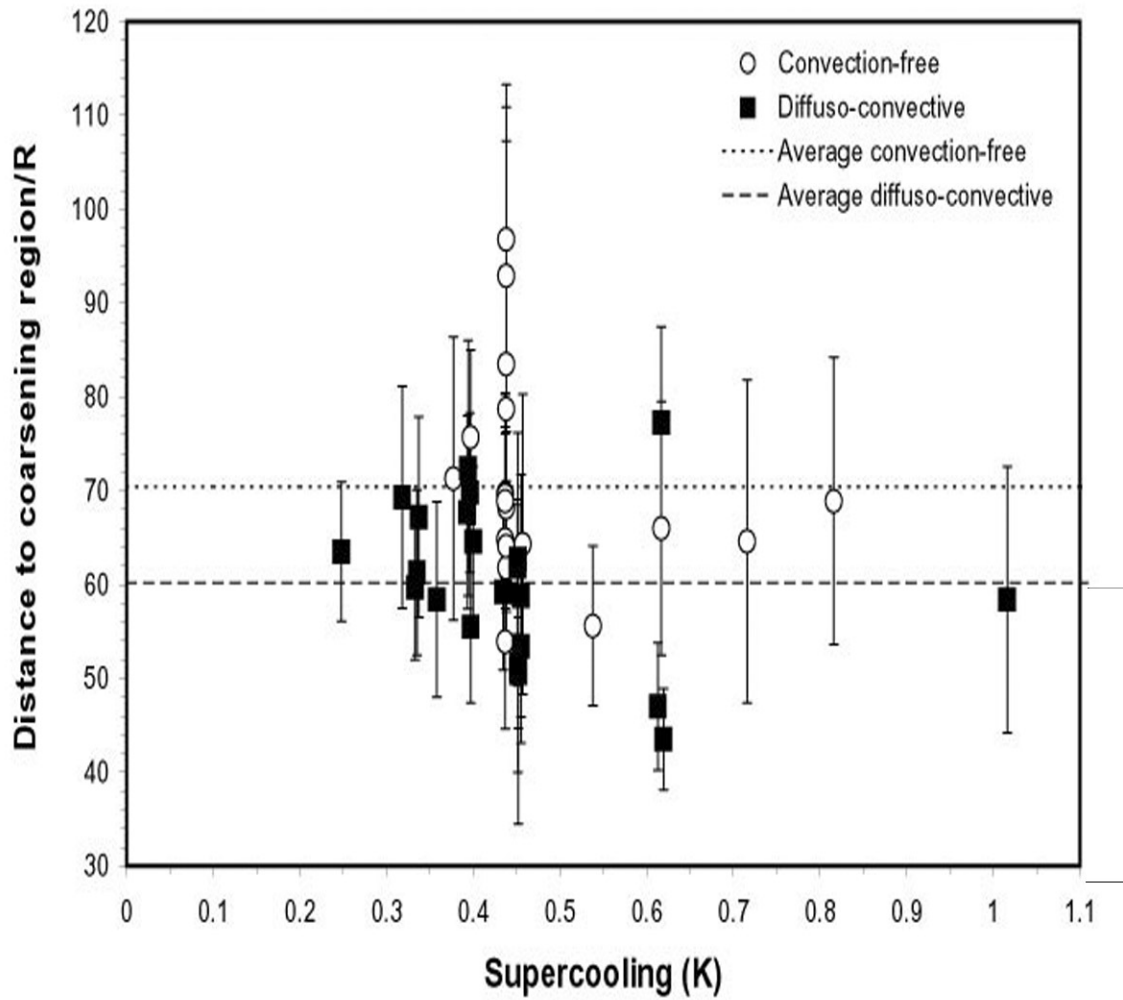


Figure 2: Distance to the first detectable coarsening normalized by the tip radius as a function of supercooling for convection-free and diffuso-convective data. There is significant statistical difference between the convection and convection-free averages.

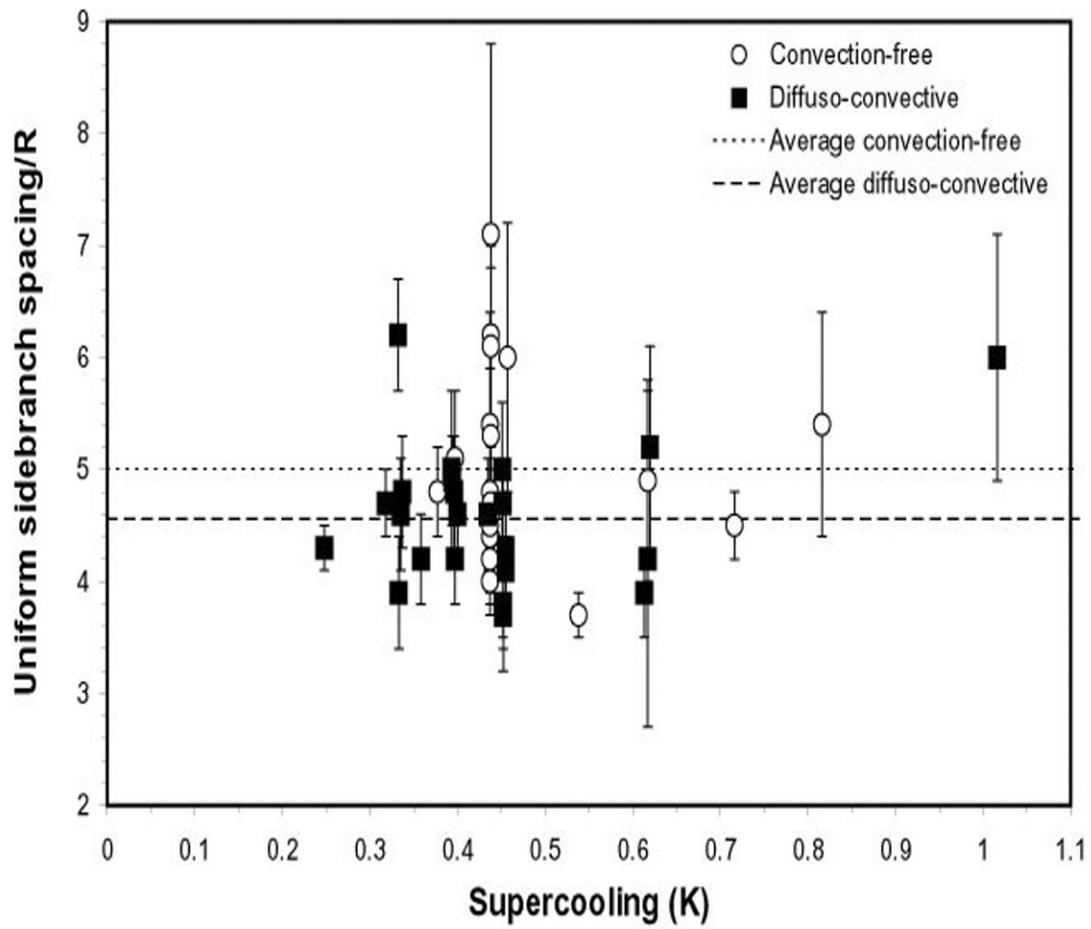


Figure 3: Sidebranch spacing in the uniform region (0-55R) normalized by the tip radius as a function of supercooling for convection-free and diffuso-convective data. There is no significant statistical difference between the convection and convection-free averages.

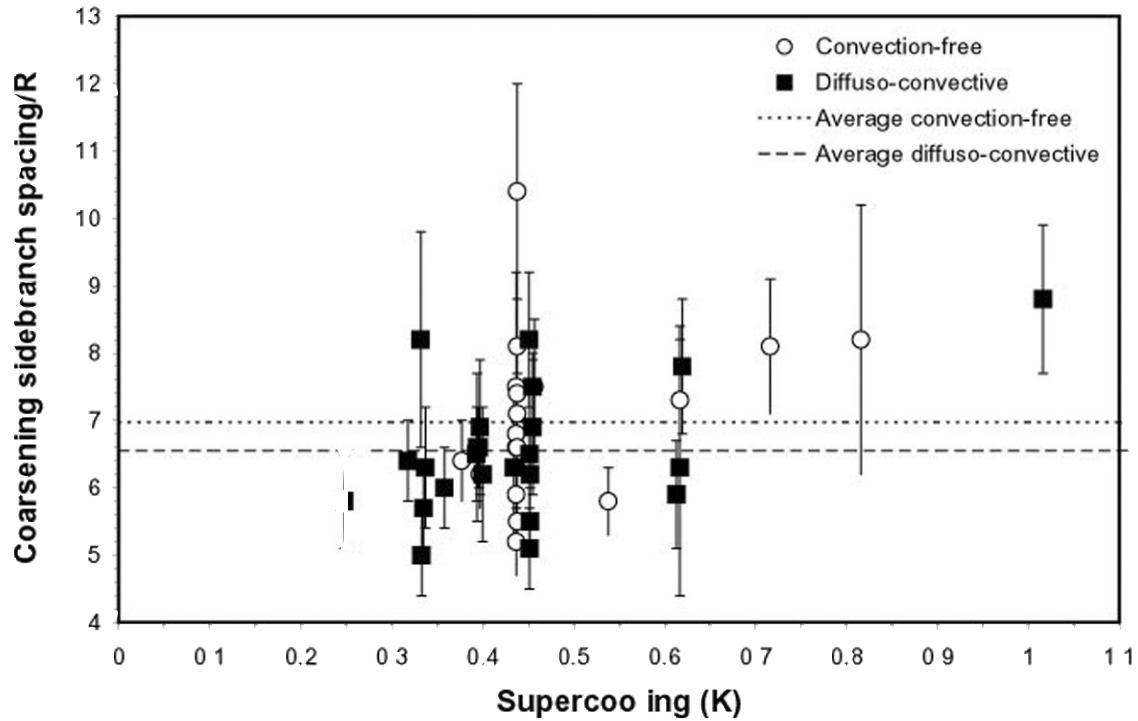


Figure 4: Sidebranch spacing in the coarsening region (55R to 200R) normalized by the tip radius as a function of supercooling for convection-free and diffuso-convective data. There is no significant statistical difference between the convection and convection-free averages.

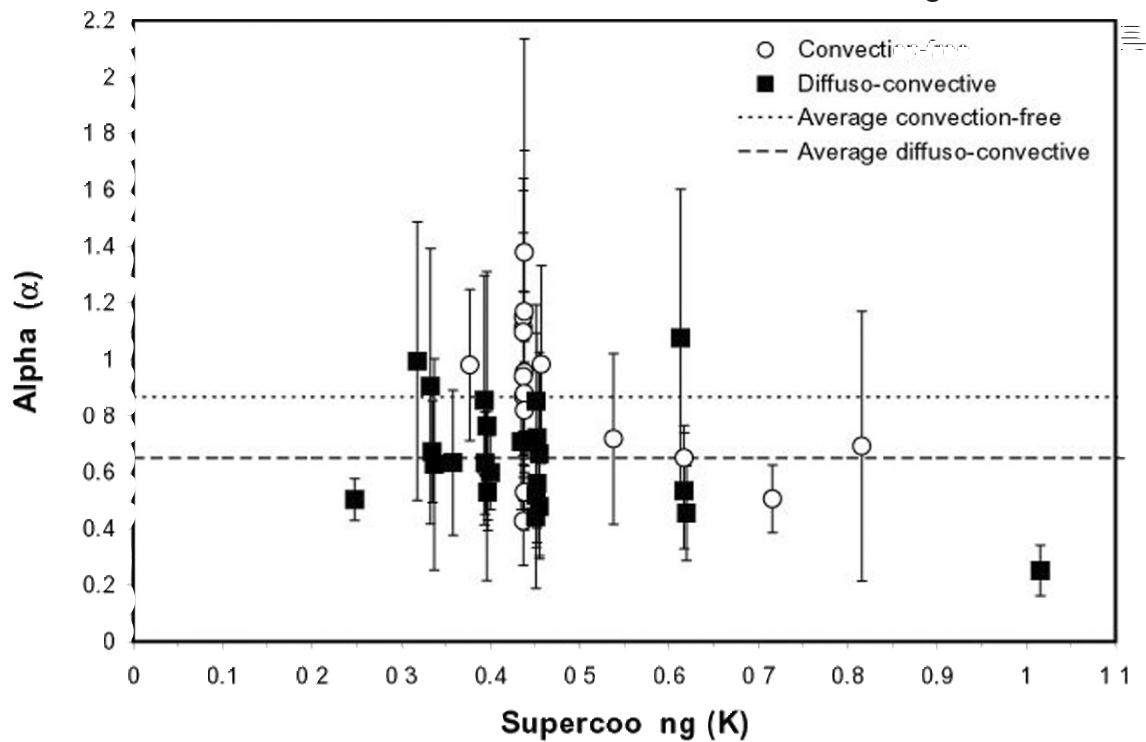


Figure 5: Pre-exponential term (α) for the sidebranch envelope as a function of supercooling for convection-free and diffuso-convective data. α appears relatively constant over this range of supercoolings and there is significant statistical difference between the convection and convection-free averages.

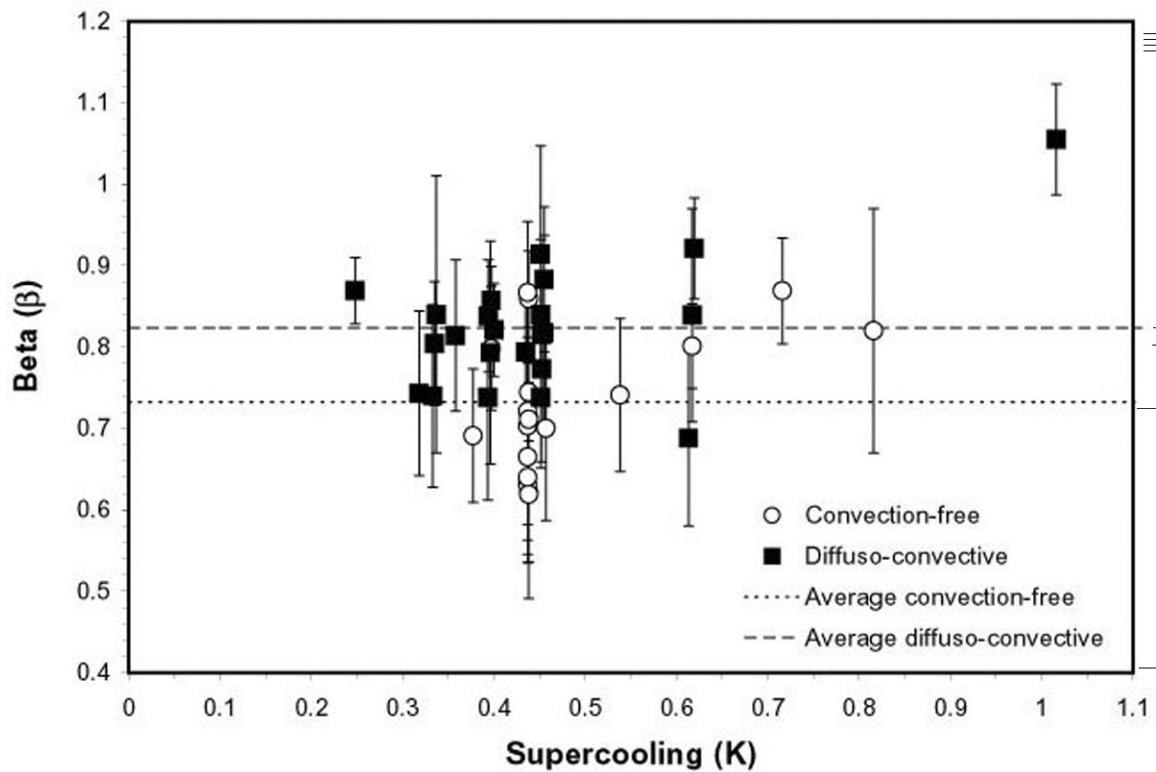


Figure 6: Exponential term (β) for the sidebranch envelope as a function of supercooling for convection-free and diffuso-convective data. β appears to be relatively constant over this range of supercoolings and there is significant statistical difference between the convection and convection-free averages.

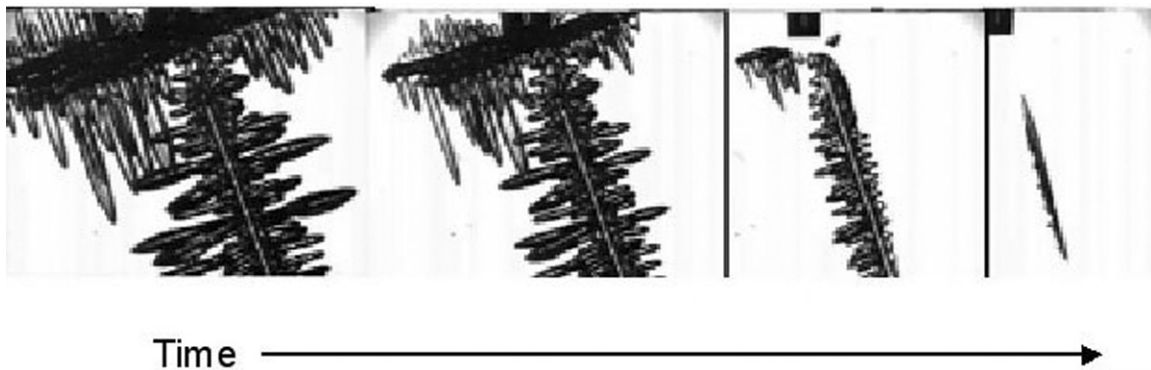


Figure 7: Video frames showing the progressive melting of a PVA dendritic mushy zone in microgravity. As the dendrites fragment, the individual crystallites remain motionless in the melt. Video data analyzed for the terminal melting of the needle crystal shown in the last panel.

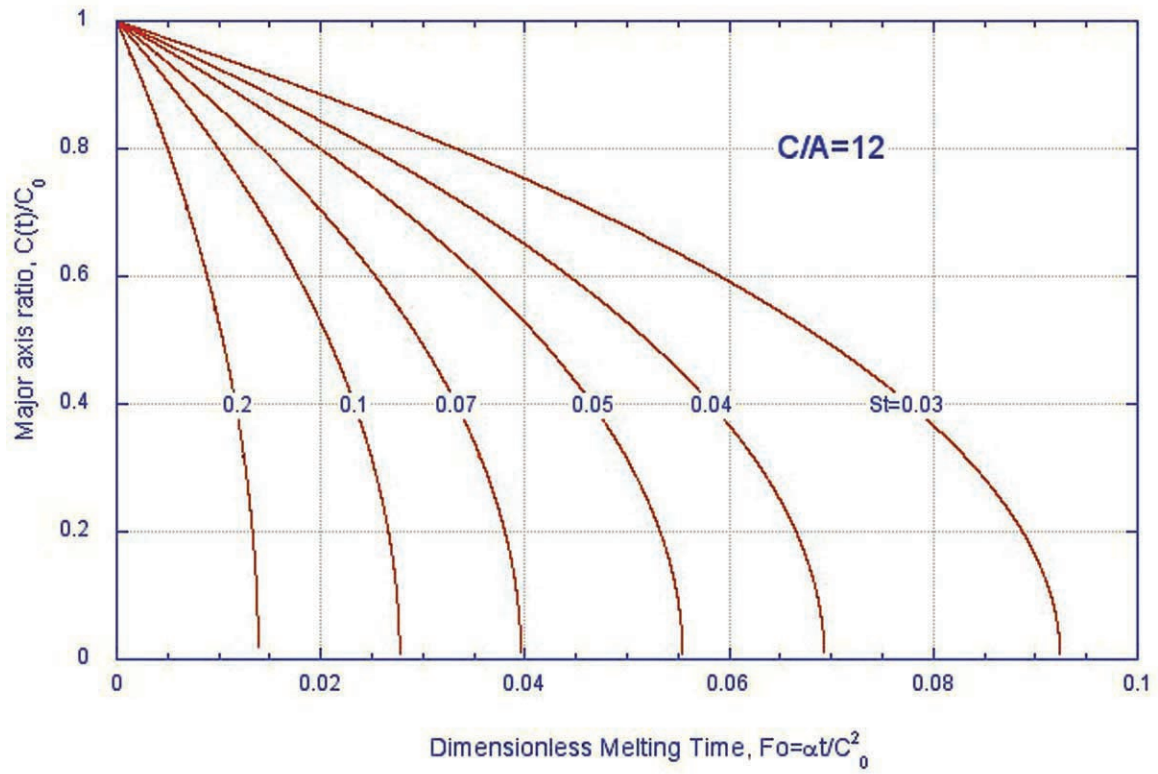


Figure 8: Major axis length scaled to initial major axis length, C/C_0 versus melting time, predicted by quasi-static approach for $C/A=12$. These curves show the sensitivity of the melting kinetics for needle-like crystal fragments to the value selected for the Stefan number.

MACROVOID DEFECT GROWTH DURING EVAPORATIVE CASTING OF POLYMERIC MEMBRANES

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Abstract

Macrovoid (MV) formation is a significant problem in evaporatively cast polymeric membranes. MVs are large, elongated or teardrop-shaped pores (~10–50 μm) that can impair membrane structural integrity. Although MVs have been extensively studied, there is no general agreement on the mechanisms governing MV growth. Recently, our research group has formulated the solutocapillary convection (SC) hypothesis, which contends that MV growth involves three principal forces: a Marangoni force generated by surface-tension gradients within the MV interface, a viscous drag force, and a gravitationally induced body force. Two sets of complementary experiments were conducted to test the SC hypothesis.

Ground-based videomicroscopy flow-visualization (VMFV) was utilized to measure the flow velocities at the MV-casting solution interface and deep within the casting solution. The measurements were performed with casting solutions containing 10 wt% cellulose acetate (CA), 30 wt% H_2O , 60 wt% acetone, and 200-ppm TiO_2 particles for flow visualization, and the surface tension was controlled by surfactant addition. Qualitatively, the experiments indicated that MV growth occurs in three distinct phases: (1) a very rapid initial growth period, (2) a much slower growth phase, and (3) absorption of selected MVs into the expanding demixed region. The presence of tracer particles inside the MVs suggests the presence of a convective flow, which transfers the particles from the bulk solution to the MV interior. Although the VMFV experiments did not establish any surfactant effect on the interfacial velocities, a statistically significant effect on the MV number density was observed.

In the second set of experiments, membranes were cast aboard a KC-135 aircraft under 0-g and 2-g conditions. Despite careful attention to the design and fabrication of the membrane casting apparatus (MCA), several problems were encountered, the most significant of which was the contamination of the casting solution by the activated carbon particles used for solvent absorption. Despite these difficulties, SEM analysis of uncontaminated membrane samples indicated that the MV morphology was strongly influenced by the solvent-nonsolvent ratio. However, dependence of MV size and number density on the magnitude of the buoyancy force could not be established since (in many cases) the MVs penetrated through the entire thickness of the cast membrane. Based upon the insights obtained from these experiments, a new MCA has been designed, which incorporates wider casting wells, deeper recesses for casting thicker membranes, and better isolation of the activated carbon. The new MCAs will be used in an upcoming KC-135 flight, and should enable complete quantitative evaluation of the SC hypothesis.

Keywords: biomaterials, polymeric membranes, membrane morphology, macrovoid growth, solutocapillary convection, buoyancy effects

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1. Introduction

Polymeric membranes can be formed via evaporative (dry) casting whereby a single-phase polymer/solvent/non-solvent (P/S/NS) solution is caused to phase-separate by evaporation of the volatile solvent. The resulting dispersed phase will ultimately become the membrane pores, whereas the continuous phase will become the solid polymer matrix of the membrane. Evaporative casting can produce macrovoids (MVs), large teardrop or finger-shaped pores ($\sim 10\text{-}50\ \mu\text{m}$) that are generally considered to be undesirable in separation applications (Figure 1). Under pressure, MVs lead to excessive compression of the porous sub-layer and possible failure of the permselective layer, thereby causing flux decline or a loss in permselectivity.¹ The methods used currently to avoid MV occurrence are largely based on trial-and-error approaches. A better fundamental understanding of MV initiation and growth would enable the development of more effective strategies for controlling their occurrence.

Although researchers have previously proposed a variety of mechanisms for MV formation, two main hypotheses are currently favored: one attributes MV growth solely to diffusion,^{2,3} whereas the other states that solutocapillary convection at the MV interface contributes to growth.⁴⁻⁷ Smolders *et al.*² and Reuvers³ state that MVs initiate when stable (i.e., outside the binodal region of the P/S/NS ternary phase diagram) polymer solution is present directly ahead of a newly formed layer of polymer-poor nuclei near the top of a freshly demixed film. They explain that after MV initiation, growth occurs by diffusion of primarily solvent to the MV nuclei, and argue that MV growth occurs when “the diffusional flow of solvent from the polymer solution into the nuclei is larger than the flow of nonsolvent from the nuclei into the polymer solution.”³ In addition, they assert that interfacial processes do not affect MV formation. Because their growth mechanism does not involve body forces, buoyancy effects cannot be accommodated in predictions of MV size. Nonetheless, as MVs grow, their increased volume could result in larger buoyancy forces. Although this hypothesis (hereafter referred to as the *diffusive growth hypothesis*) was originally formulated for wet-cast membranes, the same logic should also apply to the dry-cast process.

In contrast, the Solutocapillary Convection (SC) hypothesis⁴ contends that MV growth is governed by three principal forces: a Marangoni force generated by surface-tension gradients within the MV interface that facilitates MV growth; a viscous drag force that resists MV growth; and a gravitationally induced body force that can either resist or promote MV growth depending upon its orientation. The schematic shown in Figure 2 explains the SC hypothesis of MV growth in the dry-casting of the cellulose acetate (CA)/acetone/water system. Water has a much higher surface tension (72 dyne/cm) compared to acetone (23 dyne/cm), and our measurements indicate that in binary water/acetone mixtures the surface tension increases with increasing water fraction (Figure 3). Thus, rapid evaporation of acetone (solvent) from the gas-liquid interface causes the water (non-solvent) fraction to increase thereby generating a surface-tension gradient between the solvent-poor region near the interface, and the solvent-rich region in the bulk solution. Due to this surface-tension gradient, material along the MV/solution interface moves from the leading edge (low surface tension) to the trailing edge (high surface tension) of the MV. This process, known as solutal Marangoni (solutocapillary) convection, exerts a force on the growing MV that propels it away from the gas/liquid interface and into the underlying bulk solution. At the same time, continuity of velocities at the MV/casting solution interface causes convection cells inside the MV. The overall effect is to enhance the mass transfer of non-solvent into the growing MV. MV growth is also simultaneously opposed by a viscous drag force as well as the gravity-induced buoyant force.

In this study, we attempted to test the validity of the SC hypothesis using two different approaches in which the solutal-Marangoni and the body forces were systematically varied. In the first set of experiments, membranes were cast aboard a KC-135 aircraft that produced short durations of microgravity and 2-g conditions. The second set of experiments involved the use of videomicroscopy flow visualization (VMFV) to measure and compare the velocities at the MV-casting solution interface in solutions containing different surfactant concentrations.

We have previously reported the results of experiments in which membranes were cast in a microgravity environment aboard KC-135 aircraft.⁵ A specially designed membrane casting apparatus (MCA) suitable for microgravity casting was utilized for this purpose. However, due to several unforeseen limitations of the MCA, the membrane thickness was highly non-uniform thereby precluding any meaningful statistical analysis of the data. Qualitative observations from that study suggested that: (1) MV formation is closely linked to the S:NS ratio in the casting solution and (2) at the lowest S:NS ratio buoyancy appeared to hinder MV growth. Based upon the insights obtained from that study, the MCA was modified using (1) wider wells to obtain larger samples, (2) a different triggering mechanism to minimize sloshing, and (3) finer-machined surfaces to prevent thickness non-uniformities.

VMFV provides a direct means of measuring the interfacial velocities. However, since the membrane formation process is relatively rapid (~1-2 min) and the films typically are thin (100-500 μm), adapting flow visualization to monitor membrane casting has generally proven difficult. Recently we reported that VMFV could provide important information regarding the phenomena occurring at the MV interface.⁶ In this study, VMFV was further extended to determine the effect of a surfactant on the MV interfacial velocities. Velocities were measured at the edge of the MVs as well as in the casting solution relatively far from the MVs; in addition, MV number density data were also obtained.

2. Materials and Methods

Materials

CA with a molecular weight of 40,000 and an acetyl content of 39.8% was obtained from the Eastman Chemical Company and stored in vacuum at 80°C before use. ACS certified grade acetone obtained from Fisher was utilized in the as-received condition, and deionized water was used for making the casting solution. The surfactant employed was Triton X-100 (J. T. Baker Company). Triton X-100 (polyoxyethylene iso-octyl phenyl ether) is a nonionic surfactant with a critical micellar concentration (CMC) in water of approximately 6×10^{-3} mol/L.

Experiments aboard KC-135 aircraft

The NASA KC-135A aircraft flies in a series of parabolic maneuvers that give rise to short periods (20-25 s) of near-zero gravity in the cabin followed by a high-g pullout lasting approximately 90 s. Typical accelerations experienced during the low-g portion of flight are on the order of ± 0.02 g.

The MCA works on a sliding block principle⁷ as indicated in Figure 4. First, the casting solution is loaded into the chimneys directly over 150 μm -deep casting wells machined into a Delrin® sliding block. To initiate membrane formation, the sliding block is manually moved forward rapidly until each well is aligned directly under a chimney filled with activated carbon (suspended on a fine nylon mesh approximately 1 mm above the cast membrane). Solvent and nonsolvent then evaporate, causing phase

inversion. The MCA has six separate casting wells (1-cm diameter) and laser probes mounted on the two central wells enable solution demixing to be monitored.

A full factorial experimental design was used in these experiments in which three variables were studied: gravity induced buoyancy force (0-g or 2-g), solvent/nonsolvent mass ratio (2:1, 2.33:1, or 2.75:1), and surface tension (using surfactant-free and surfactant-containing solutions). In order to optimize use of the limited time of low-g available, 1-g membranes were cast on the ground in the MCA.

The casting solutions were prepared one day prior to the flight and stored in vials. Solutions to be cast on board the KC-135 were loaded in 1-cc syringes (Benton-Dickinson #309602) less than 1 hr before flight. Shortly after takeoff, the solutions were transferred to and sealed in the MCA (gravimetric measurements indicated that solvent-vapor leakage from the apparatus was insignificant when solutions were stored in syringes for fewer than 3 hr and in the MCA for less than 1 hr). In microgravity, the MCA was allowed to free-float in the aircraft cabin such that each nascent membrane experienced at least 25 s of zero gravity immediately after casting. All samples were dried for at least 2 hr prior to removal from the MCA. Scanning electron micrographs of the cross-sections of all membranes were obtained using a RJ Lee PSEM scanning electron microscope.

Videomicroscopy Flow Visualization

For the VMFV experiments, casting solutions containing 0, 31.4, 300, and 3000 ppm Triton-X surfactant were used. The solutions were stirred vigorously for several hours and taken off the stir plate 30 min prior to the experiments to allow entrained air bubbles to escape from the solution. A small amount of tracer particulates – 200 ppm of TiO_2 particles – was added to the casting solution to facilitate visualization of the microscopic flows. Although the individual TiO_2 particles were only a few nanometers in diameter, they typically formed aggregates, which were in some cases as large as 1 micron.

Figure 5 shows a schematic of the VMFV experimental arrangement. Using a syringe, the casting solution was injected into the space between two microscope slides separated by a Teflon shim until the solution reached a barrier (pin). The pin helped in isolating the casting solution from the air, and also provided a constant diffusion length of 1 cm between the solution/air interface and the leading edge of the microscope slides. Contact between the casting solution and the air was initiated by removing the pin. The preferential evaporation of acetone upon contact of the solution with air led to solution demixing and membrane formation. As shown in Figure 5, the casting solution had two interfaces with air – the front and the rear interface. Since evaporation from the rear interface could confound the experiment by affecting the bulk flows, a drop of acetone was inserted close to the rear interface – the vapor pressure generated by the drop significantly reduced evaporation from the rear interface.

The demixing front and the MVs were tracked using a video microscope. A CCD camera with a view window of 730×550 microns was attached to a video microscope, and recorded images at 1 s intervals. The PC software Scion Image⁸ was used for the flow visualization analysis. Typically, tracer particles close to the MV interface were tracked over five frames to obtain the MV interfacial velocities. Wherever possible, two particles were tracked at the MV edge, and the average of the two velocities was used as the “raw” edge velocity. Similarly, four tracer particles far from the MV but at almost the same distance from the demixing front were chosen and tracked for five frames and the “raw” bulk velocity was obtained by averaging these four velocities. The leading edge of the MV was also tracked during the same time interval to obtain the MV velocity, which was then subtracted from the raw velocities to obtain the actual

edge and bulk velocities. Only those MVs whose size stayed relatively constant during the time interval were considered for the computation of the edge velocities. In this fashion, the artifacts associated with the growth/shrinkage of the MVs were minimized. The edge velocity ratio (EVR) was calculated by dividing the edge velocity by the bulk velocity. In addition to measuring the particle velocities, the number of the MVs seen in the viewing frame was also determined.

3. Results

Microgravity and 2-g experiments

The parabolic maneuvers of the KC-135 aircraft only produce relatively short intervals of 0-g and 2-g, and it was necessary that the entire casting solution demix within this interval. Light reflection measurements using the two laser probes confirmed that complete demixing did occur within 20 s. Although the membranes prepared in the new MCA were larger and more uniform in thickness compared with those of an earlier study, some problems were still encountered. In some instances, the nylon mesh holding the graphite particles tore and the particles dropped into the casting solution, affecting the membrane morphology. In other cases, the MCA had to be hand-held during the microgravity maneuver, and hence did not free-float. As a result, only a limited number of “good” membrane samples were available for analysis.

Since the buoyancy force opposes MV growth, one would expect the MVs formed in 0-g to penetrate deeper into the membrane (thickness direction) as compared to those formed in 2-g. In contrast, adding the surfactant should reduce MV penetration because of the smaller surface-tension gradient. However, the limited time interval of 25 s for demixing restricted the initial film thickness. Consequently, in most cases the MVs penetrated through the entire membrane thickness. Figures 6 and 7 show the influence of the surfactant (at 2-g) and the buoyancy force, respectively, on the MV size (average MV area) at two different S:NS ratios. These data do not indicate a statistically significant dependence of MV size on the surfactant concentration or the buoyancy force, most likely due to the penetration of the MVs through the entire thickness of the cast membrane.

Videomicroscopy experiments

The viscosities of casting solutions with and without the 200-ppm TiO_2 tracer particulates were measured and found to be statistically identical. Thus, a change in the MV formation hydrodynamics associated with a difference in viscosities was not a concern for the VMFV experiments. Information regarding the effect of the surfactant on the casting solution surface tension would also be valuable; this becomes particularly important in view of the fact that the surface tension of the ternary solution cannot be predicted on an *a-priori* basis even though the CMC of Triton X-100 in water is known. However, this measurement is difficult because of high casting-solution viscosity and rapid acetone evaporation from the gas/solution interface. In addition, the surfactant concentration in the compositions utilized is diluted since water comprises only 30 wt% of the solution. Consequently, surfactant concentrations that differed by an order of magnitude (30, 300, and 3000 ppm in water) were selected for this study.

Figures 8 and 9 show the effect of surfactant concentration on the EVR and the MV density, respectively. Analysis of the EVR data via standard analysis of variance techniques indicated that there was no statistical difference among the four cases, *i.e.* 0, 31.4, 300, and 3000 ppm of Triton X-100. On the other hand, analysis of the MV density data indicated that there was a statistically significant difference among the groups. A multiple comparison procedure established that the number density of MVs with a casting solution containing 300-ppm surfactant was distinct from that for a surfactant-free casting solution.

Observations during the experiments indicated that in most cases, the MVs grew “explosively” from the demixing front (within 2-3 s). Over time, tracer particles became visible inside the MVs. This is a particularly significant observation, since the presence of tracer particulate inside the MVs cannot be explained by diffusion, and thus suggests the presence of a convective flow that enables transfer of the particles from the bulk solution into the MVs.

4. Discussion

In a previous study,⁶ a scaling analysis was conducted to compare the magnitudes of the buoyancy and viscous drag forces for a MV approximately 50 microns in diameter. This analysis indicated that the buoyancy force is much smaller than the viscous drag force. Additionally, while the viscous drag force is proportional to the MV radius, the buoyancy force is proportional to its third power, thus implying that in the initial growth phase, the buoyancy force would be negligibly small compared to the viscous drag force. However, the viscous drag force depends upon the velocity of the growing MV; whereas this force would be significant in the initial growth phase of the MV, it would diminish to zero in a fully grown MV. Therefore, the buoyancy force can indeed become significant in determining the final size and shape of the MV. However, for the buoyancy effect to be significant, the MV must be sufficiently large (~ 80-100 μm).

In the present experiments at the lowest S:NS ratios, MVs penetrated through the entire membrane thickness under 0-g as well as 2-g conditions. Hence, the effect of buoyancy or surface tension could not be validated. Our calculations indicate that such validation would require a much greater initial casting solution thickness (~ 500 μm).

Although the VMFV results indicated that the presence of surfactant did have a statistically significant effect on the MV density, the EVR was not significantly altered. This result appears to imply that the relationship between solutocapillary convection and MV growth is tenuous. However, several important factors must be considered in interpreting these results. First, the drag forces on the particulate aggregates (assumed negligible) might have been significant and second, not all of the “interfacial particles” were exactly at the MV/solution interface. Hence, these particles might not have accurately tracked the actual edge velocity. Furthermore, velocities were tracked only during the mature phase of the MV growth process in order to avoid the artifacts associated with MV rapid growth/shrinkage. At this point in the MV growth process, the concentration gradients might already have become too small to be of significance. Finally, the overall hydrodynamics in the VMFV arrangement are different from “usual” membrane casting conditions in that the former has a vertical face exposed to air and the demixing front moves horizontally.

Nonetheless, observations during the VMFV experiments yielded important information about MV growth via the observation of tracer particulate inside the MVs. Their presence cannot be explained either by diffusion or by the SC hypothesis, and strongly implies the presence of a convective flow that transports the particles from the bulk solution to the interior of the MVs. This occurrence suggests that multiple mechanisms may be associated with MV growth. This possibility is reinforced by the observation that although the surface tension gradient during the subject CA membrane casting is significant, MVs are also observed in systems where the surface tension difference between the solvent and non-solvent is not very large.³ Hence, whereas solutocapillary convection may well facilitate MV growth in the CA/acetone/water system, this phenomenon may not generally represent the principal mechanism driving MV growth.

5. Future Work

While the KC-135 and VMFV experiments have provided new and intriguing data regarding the formation and growth of MVs, the results did not provide complete statistical evidence for the influence of solutocapillary convection on the MV growth process. Indeed, results from both the KC135 and VMFV experiments indicate that MV growth is a complex process and emphasize the need for additional studies that employ more sophisticated approaches. We have recently fabricated a new MCA based on a modified design. The new MCA incorporates solid carbon monoliths for absorbing volatile solvent (acetone). This approach should eliminate the problem of carbon particles falling into the casting solution. Also, the new MCA has a movable aluminum substrate that will enable controlled variation of the casting solution thickness and facilitate removal of the final membrane. Water-holding compartments facilitate a wet-casting option. The new MCA will be extensively tested on the ground (1-g) prior to future KC-135 flights to identify the set of parameters including casting solution concentration and initial film thickness that will provide partial MV penetration. These parameters will then be used to cast membranes aboard the KC-135 at 0-g, 1-g and 2-g. The use of multiple MCAs for the KC-135 casting experiments should enable us to obtain a much more extensive database that can provide complete quantitative evidence regarding the significance of SC convection on MV growth.

Acknowledgements

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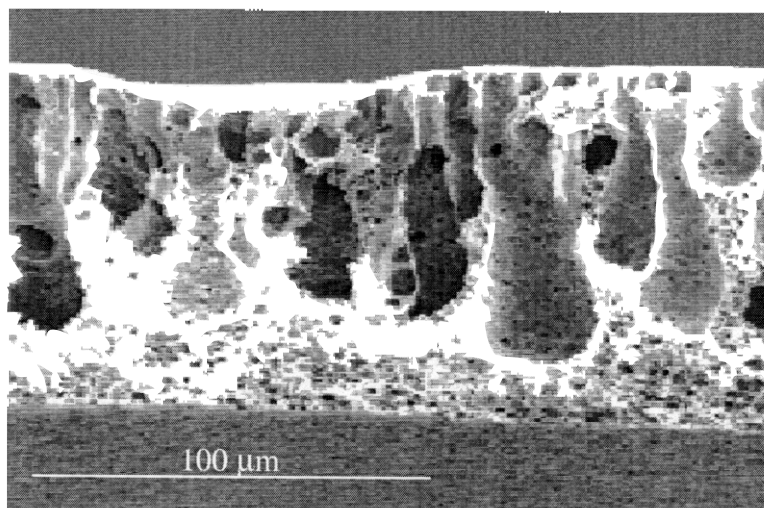


Figure 1. Cross-section of a membrane cast from a CA/acetone/water solution showing the presence of macrovoids.

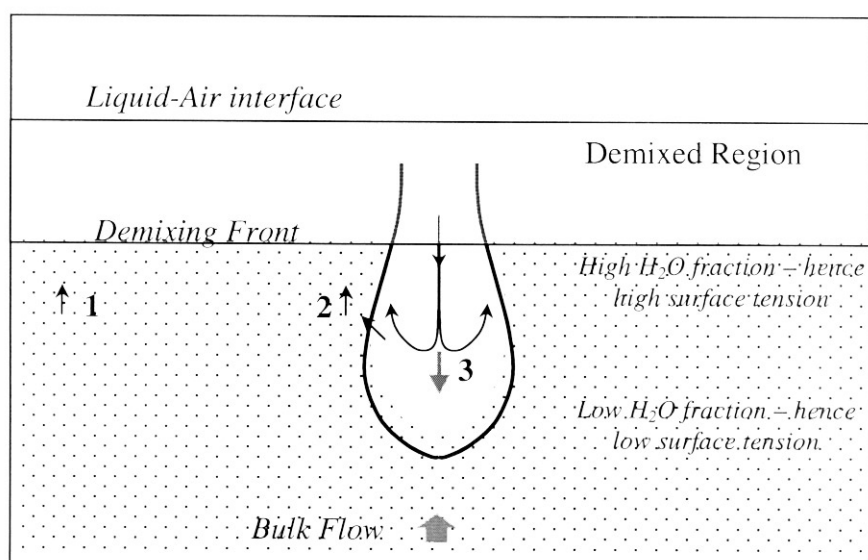


Figure 2. Schematic explaining the SC mechanism for MV growth. The surface-tension gradient induces an interfacial flow at the MV interface, which in turn induces a bulk flow in the surrounding solution. The velocities at points 1, 2, and 3 refer to the far-field, MV interface, and MV velocities, respectively. The EVR is calculated as $EVR = (v_2 - v_3) / (v_1 - v_3)$. The SC mechanism predicts that EVR would decrease if surfactants were added to the casting solution.

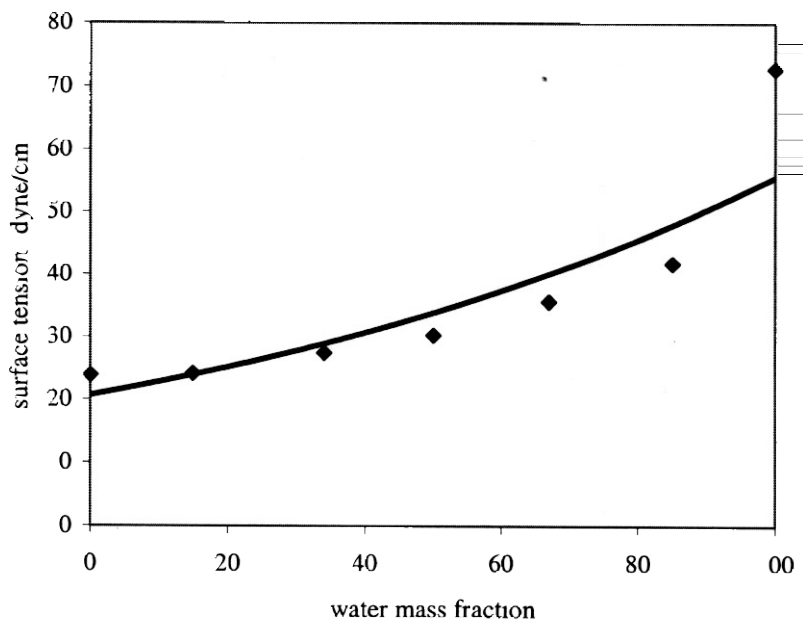


Figure 3. Variation in the surface tension of binary water/acetone solutions with increasing water mass fraction.

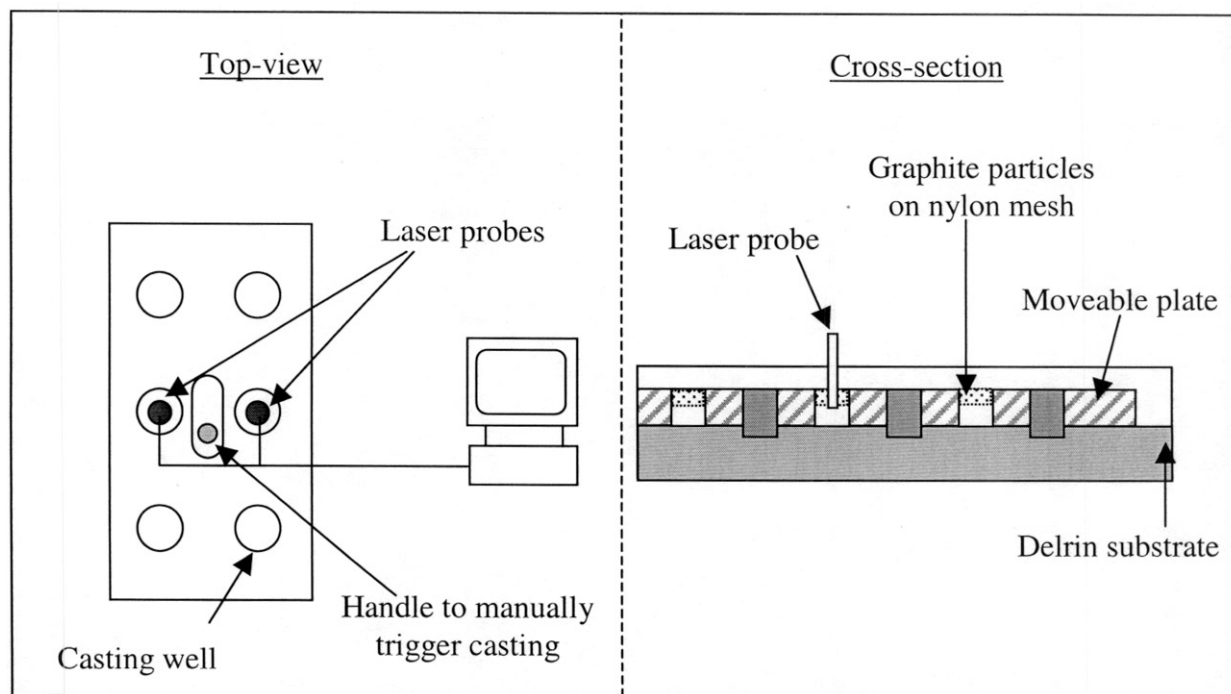


Figure 4. Schematic of the membrane casting apparatus (MCA).

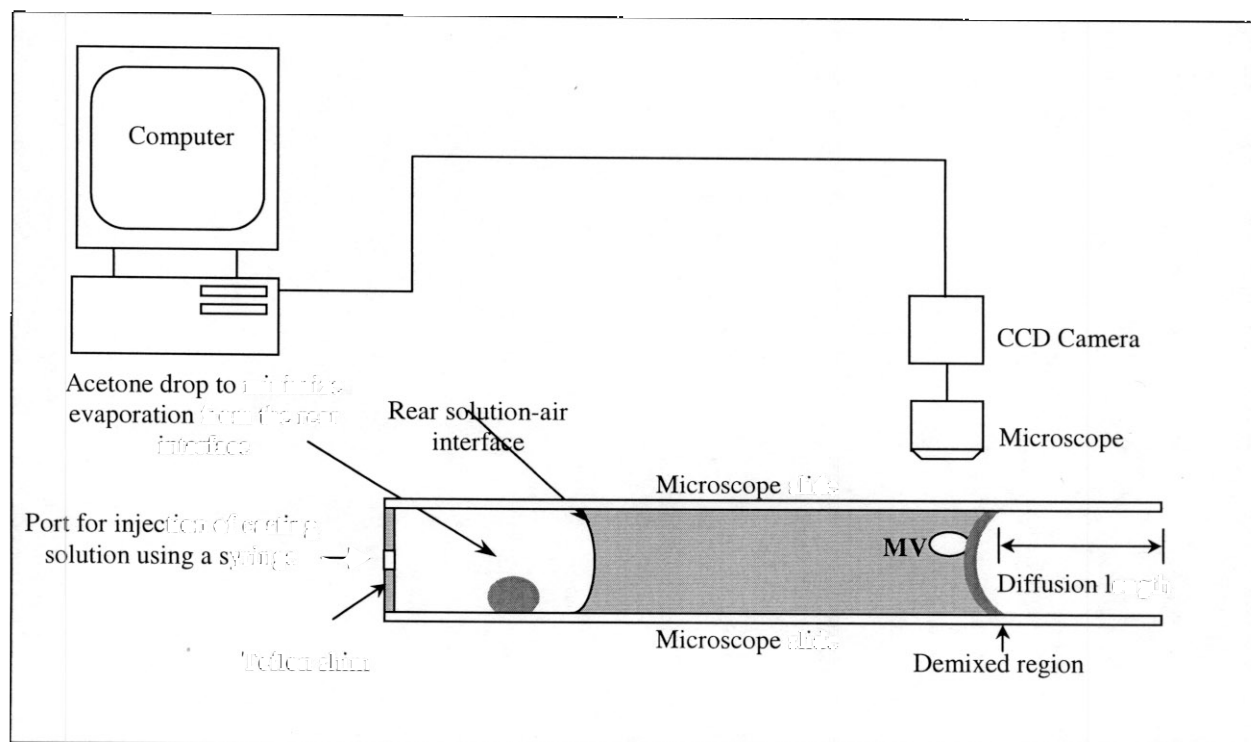


Figure 5. Schematic of the videomicroscopy set-up. The casting solution is inserted between two microscope slides that are separated by Teflon shims. The small “bulb” at the left of the demixing front is a macrovoid.

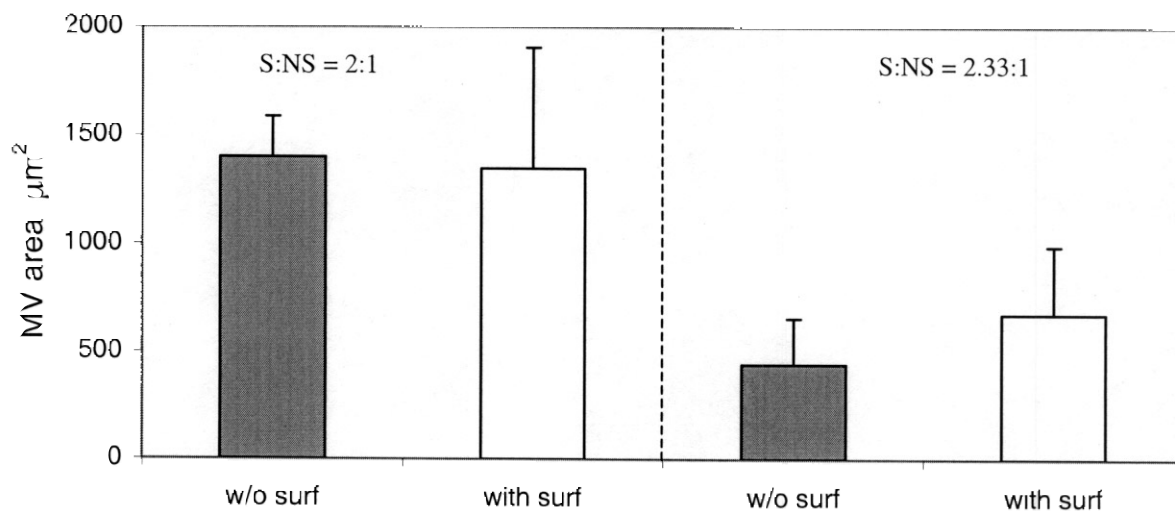


Figure 6. Influence of surfactant on the MV size at different S:NS ratios under 2-g conditions. Overall, the MV size decreases with the S:NS ratio but the surfactant does not appear to affect MV size.

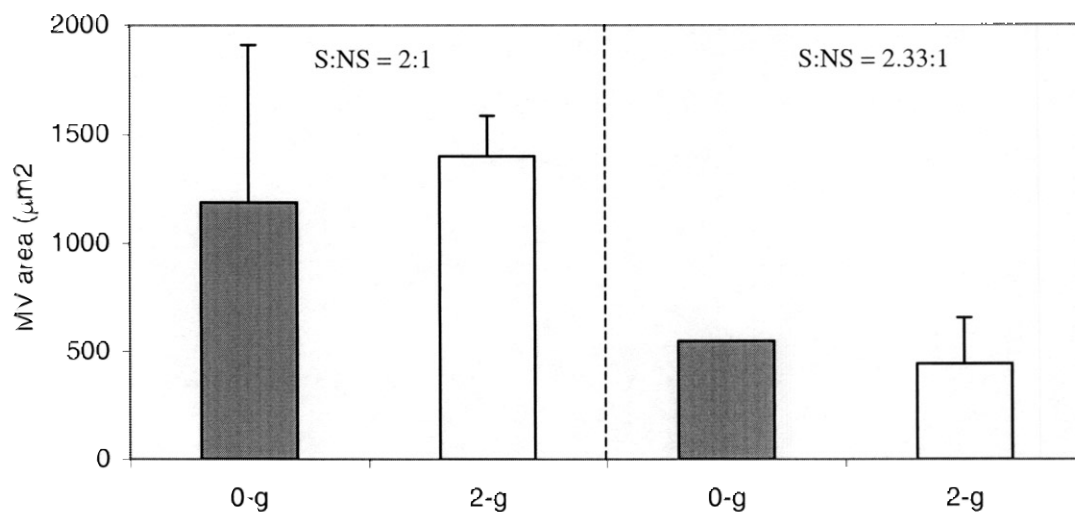


Figure 7. Influence of buoyancy on the MV size for two different S:NS ratios. Buoyancy does not appear to affect MV size.

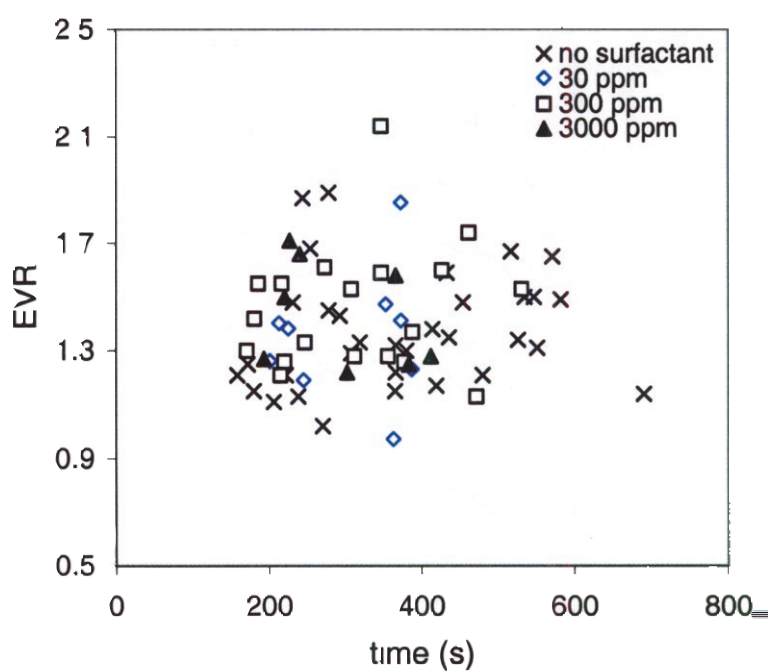


Figure 8. Influence of surfactant concentration on the EVR. No systematic trends were observed.

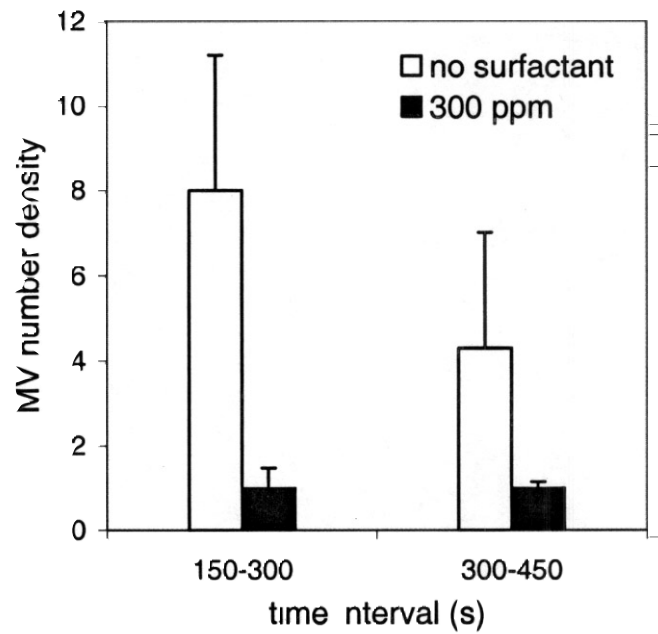


Figure 9. Influence of surfactant concentration on the MV number density, defined as the number of MVs viewed in a single frame.

TOWARD UNDERSTANDING PORE FORMATION AND MOBILITY DURING CONTROLLED DIRECTIONAL SOLIDIFICATION IN A MICROGRAVITY ENVIRONMENT INVESTIGATION (PFMI)

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The generation and inclusion of detrimental porosity, e.g., “pipes” and “rattails” can occur during controlled directional solidification processing. The origin of these defects is generally attributed to gas evolution and entrapment during solidification of the melt. On Earth, owing to buoyancy, an initiated bubble can rapidly rise through the liquid melt and “pop” at the surface; this is obviously not ensured in a low gravity or microgravity environment. Clearly, porosity generation and inclusion is detrimental to conducting any meaningful solidification-science studies in microgravity. Thus it is essential that model experiments be conducted in microgravity, to understand the details of the generation and mobility of porosity, so that methods can be found to eliminate it. In hindsight, this is particularly relevant given the results of the previous directional solidification experiments conducted in Space.

The current International Space Station (ISS) Microgravity Science Glovebox (MSG) investigation addresses the central issue of porosity formation and mobility during controlled directional solidification processing in microgravity. The study will be done using a transparent metal-analogue material, succinonitrile (SCN) and succinonitrile-water “alloys”, so that direct observation and recording of pore generation and mobility can be made during the experiments. Succinonitrile is particularly well suited for the proposed investigation because it is transparent, it solidifies in a manner analogous to most metals, it has a convenient melting point, its material properties are well characterized and, it has been successfully used in previous microgravity experiments. The PFMI experiment will be launched on the UF-2, STS-111 flight.

Highlighting the porosity development problem in metal alloys during microgravity processing, the poster will describe: (i) the intent of the proposed experiments, (ii) the theoretical rationale behind using SCN as the study material for porosity generation and migration and, (iii) the experimental protocol for the investigation of the effects of the processing parameters. Photographs of the flight experimental hardware, and the novel sample ampoule, will be exhibited. The experimental apparatus will be described in detail and a summary of the scientific objectives will be presented.

Keywords: ISS glovebox, succinonitrile, directional solidification, porosity, microgravity, flight

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INTER-DIFFUSION IN PBO - SiO₂ MELTS: EFFECT OF FREE CONVECTION

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Understanding the kinetics of a variety of technologically important processes such as crystal growth, homogenization, and phase separation requires accurate measurements of the interdiffusion coefficients. Accurate measurements of diffusion coefficients are also needed for developing an understanding of the relationship between the structure and transport properties of liquids and melts. However, earth-based measurements of interdiffusion coefficients in liquids are not easy to perform since diffusion profiles of composition are perturbed by natural convection which is caused by composition induced density changes. The solutal convection cannot be completely eliminated since it is intrinsically linked with compositional changes. One possible solution is to carry out experiments in zero-gravity environment. Another is to quantify and to account for the effect of solutal convection on interdiffusion composition profiles. Several quantitative analyses are available in the literature. To test these theoretical results, it is necessary to generate reliable experimental data in simple binary systems.

We have performed experiments in lead silicate super-cooled melts (40 and 50 mol% PbO) since the diffusion profiles can be quenched to room temperature where they can be measured conveniently by electron analytical techniques. Two types of interdiffusion infinite couples with the inter-diffusion direction same as the direction of gravity were annealed at 750 and 850° C for various times. In normal couples, the low density melt (40 mol % PbO) was on top and in inverted couples the high density composition (50 mol % PbO) was on top. No free convection is expected in the normal couples and these profiles can be used to obtain the true values of the diffusion coefficients. Free convection is expected in the inverted couples. The profiles for the inverted couples can be used to test the validity of the models.

In all (except one) experiments with inverted couples a complete inversion of the compositions was observed indicating that the Rayleigh-Taylor instability was dominant. The Rayleigh-Taylor instability describes the inversion of two immiscible liquids when the heavier one lies on top. However, one couple did not show inversion and was only in the early stages of Rayleigh-Taylor instability. We were able to measure the composition profiles in this couple at several different locations. The results and analysis of these experiments will be presented.

Keywords: inter-diffusion, solutal convection, lead silicate melts, new research

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SECONDARY NEUTRON PRODUCTION FROM SPACE RADIATION INTERACTIONS: ADVANCES IN MODEL AND EXPERIMENTAL DATA BASE DEVELOPMENT

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For humans engaged in long-duration missions in deep space or near-Earth orbit, the risk from exposure to galactic and solar cosmic rays is an important factor in the design of spacecraft, spacesuits, and planetary bases. As cosmic rays are transported through shielding materials and human tissue components, a secondary radiation field is produced. Neutrons are an important component of that secondary field, especially in thickly-shielded environments. Calculations predict that 50% of the dose-equivalent in a lunar or Martian base comes from neutrons, and a recent workshop held at the Johnson Space Center concluded that as much as 30% of the dose in the International Space Station may come from secondary neutrons. Accelerator facilities provide a means for measuring the effectiveness of various materials in their ability to limit neutron production, using beams and energies that are present in cosmic radiation. The nearly limitless range of beams, energies, and target materials that are present in space, however, means that accelerator-based experiments will not provide a complete database of cross sections and thick-target yields that are necessary to plan and design long-duration missions. As such, accurate nuclear models of neutron production are needed, as well as data sets that can be used to compare with, and verify, the predictions from such models. Improvements in a model of secondary neutron production from heavy-ion interactions are presented here, along with the results from recent accelerator-based measurements of neutron-production cross sections.

An analytical knockout-ablation model capable of predicting neutron production from high-energy hadron-hadron interactions (both nucleon-nucleus and nucleus-nucleus collisions) has been previously developed. In the knockout stage, the collision between two nuclei result in the emission of one or more nucleons from the projectile and/or target. The resulting projectile and target remnants, referred to as prefragments, then decay by the emission of nucleons, composites, and gamma rays. Recent improvements to the model have incorporated coalescence effects, which effectively tie up single nucleons in the formation of composites during final-state interactions. Comparison of the improved model's predictions with neutron production data near 0° in the $^{40}\text{Ca} + \text{H}$ reaction at 357 and 565 MeV/nucleon show marked improvement.

Keywords: cosmic radiation, secondary neutron production, knockout-ablation model, radiation

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TWINNING, EPITAXY AND DOMAIN SWITCHING IN FERROELASTIC INCLUSION COMPOUNDS

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Our research is in the area of solid-state organic chemistry, which lies at the interface between physical organic chemistry and materials science. We use crystalline solids as models to probe fundamental issues about physical processes, molecular interactions and chemical reactions that are important for fabrication, stabilization and application of technological materials. Much of our most recent work has focused on the phenomena of ferroelastic and ferroelectric domain switching,¹⁻² in which application of an external force or electric field to a crystal causes the molecules inside the crystal to reorient, in tandem, to a new orientational state (Figure 1).

To better understand and control the domain switching process, we have designed and synthesized over twenty closely related, ferroelastic organic crystals. Our approach has been to use crystalline inclusion compounds, in which one molecule (the guest) is trapped within the crystalline framework of a second molecule (the host). By keeping the host constant and varying the proportions and kinds of guests, it has been possible to tailor these materials so that domain switching is rapid and reversible (which is desirable for high technology applications). Inclusion compounds therefore serve as powerful systems for understanding the specific molecular mechanisms that control domain switching.

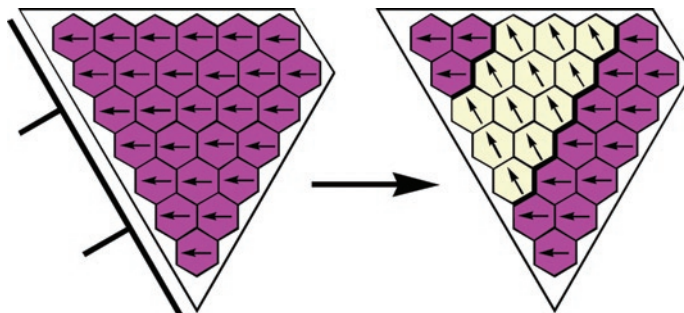


Figure 1. Schematic representation of irreversible ferroelastic domain switching in a crystal that is distorted from hexagonal symmetry. (For 2,10-undecanedione/urea, the arrows represent one layer of guest carbonyls and the principal component of the strain in this antiferroelectrically ordered material.) Before stress (left), the crystal is in the extinguishing position and appears magenta when viewed between crossed polars and a λ plate. After stress (right), a large domain has been reoriented by approximately 60° about the channel axis. Concomitant reorientation of the optical indicatrix allows transmission of light, and for thin crystals, a shift toward yellow interference colors.

Much of our work has focused on a series of urea inclusion compounds containing alkanediones such as 2,10-undecanedione (see Figure 2). These inclusion compounds are channel structures in which the guest is trapped within a honeycomb framework of host molecules. The urea host forms a well-defined helical

Keywords: ferroelastic, inclusion compound, birefringence, twinning, epitaxy, new research

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network of hydrogen bonds that surround the long chain guest molecules, which are packed within van der Waals contact along the channel axis. Although many urea inclusion compounds occur as high-symmetry, incommensurate (nonstoichiometric) structures, certain alkanediones form commensurate structures in which the urea turns into the channel to form hydrogen bonds between its syn N-H group and the carbonyl of the guest. For guests with channel axis repeats that are integer or half-integer multiples of the repeat of the urea helix, guests within a channel are related by either translation or twofold screw axes, and the inclusion compounds form low symmetry structures that can exhibit ferroelastic domain switching. In the case of 2,10-undecanedione/urea, there are two guests for every three turns of the urea helix, and the guests within a channel are related by twofold screw axes. This crystal is orthorhombic with space group $C222_1$.

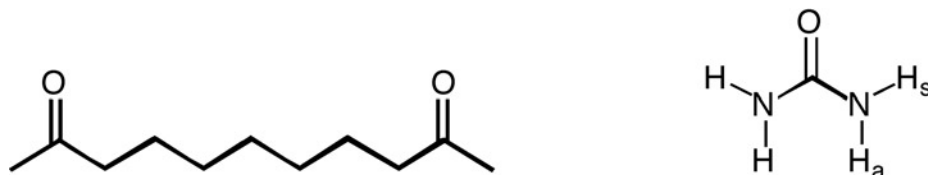


Figure 2. Chemical structures for the guest (2,10-undecanedione) and host (urea), which form a channel inclusion compound with the stoichiometry of one guest for nine host molecules. On the urea, syn and anti hydrogens are designated H_s and H_a .

Application of external anisotropic stress to a $\{110\}$ face of 2,10-undecanedione/urea gives rise to a ferroelastic domain reorientation, as depicted in Figure 1. In this helical inclusion compound, several events are required for the domain switching process to occur. When stress is applied to the left side of this crystal (as shown in Figure 3), the guests must rotate in a clockwise fashion about their long axes to relieve the stress. As they rotate, the guests break their hydrogen bonds to the host, and the host molecules, in turn, rotate back into alignment along the vertical channel wall ((100)). In order to establish the new (daughter) domain, the guests must translate up the channel axis by $1.84 \text{ \AA}$ and form hydrogen bonds with the next urea in the helix (which rotate into the channel). In the left-handed helical structure shown in Figure 3, clockwise rotation of the guests requires that the guests progress out of the plane of the figure and toward the viewer. In the same manner, stress applied to the lower right $\{110\}$ face of the same crystal gives rise to a counterclockwise rotation of the guest molecules. To establish the daughter domain, the guests would progress down the channel (away from the viewer) to the next available urea in the helical structure. In an enantiomorphic crystal (containing a right handed helix), the direction of progression would be the opposite.

Crystals of 2,10-undecanedione/urea and related materials ordinarily grow as twinned crystals containing several sectors. In such crystals, which are distorted significantly from hexagonal metric symmetry, twinning can occur across $(130)(130)$ or $(110)(110)$ boundaries (Figure 4). As shown by synchrotron white beam X-ray topography,³ these are unstrained twin boundaries in which the two adjacent domains are epitaxially matched with each other. In other words, for each boundary, the projection of the strain for a given domain onto the twin boundary is equal to that for the adjacent domain. Local disorder occurs at the twin interface because the network of host-guest hydrogen bonds is disrupted, but only unstrained twin boundaries are allowed in crystals with significant distortion.

These rotational twins can be observed quite readily with a polarizing microscope containing a compensator (λ plate). Because the crystal is distorted significantly along $[100]$, the crystals are biaxial and have significant birefringence when viewed down the channel axis. For thin crystals, it is possible to observe interference colors, which differ for the differently oriented domains (Figure 5). Thicker crystals do not

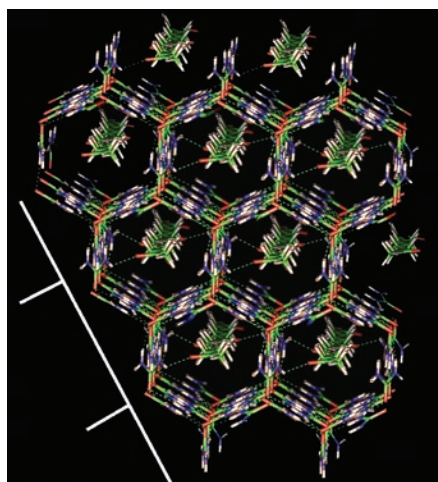


Figure 3. Channel axis view of 2,10-undecanedione/urea showing orientation of applied stress (a horizontal, b vertical). This structure contains a left-handed urea helix, as defined by the chain of $\text{C}=\text{O} \cdots \text{H}_\text{a}-\text{N}$ hydrogen bonds. Guest molecules are related by a twofold screw axis along the channel, and their mean planes lie near the (010) plane.

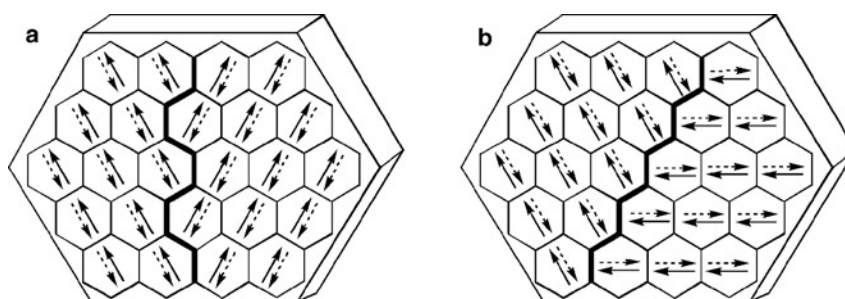


Figure 4. (a) Schematic diagram of twinning across a (130)(130) boundary. Note that this allowed twin boundary is perpendicular to the $\{110\}$ face of the crystal and that the strain on each side of this domain wall is projected onto the boundary in an equivalent manner. (The guest carbonyls and the $[100]$ axes make approximately 30° angles with the boundary.) (b) Twinning across a (110)(110) boundary. Again, there is no strain because within each sector, $[100]$ makes the same angle of approximately 60° with the twin boundary.

exhibit interference colors in the visible region of the spectrum, but they do exhibit characteristic extinction orientations. In addition to the observable rotational twinning, urea inclusion compounds are known to exhibit chiral twinning in which right and left handed helical structures are formed within the same crystal.⁴ For strongly birefringent crystals such as 2,10-undecanedione/urea this type of twinning is ordinarily invisible because the linear birefringence is orders of magnitude larger than the optical rotation.

It is now possible to quantitatively map the orientation and magnitude of a crystal's birefringence using a Metripol microscope.⁵ This device utilizes a rotating polarizer- $\lambda/4$ plate-analyzer to map the birefringence for each pixel in an image. In the experiment, intensity maps are collected for a series of polarizer orientations, and a Fourier analysis of the intensity variation gives rise to three maps: intensity, indicatrix orientation and retardation. With small retardations, data collected at one wavelength are sufficient to

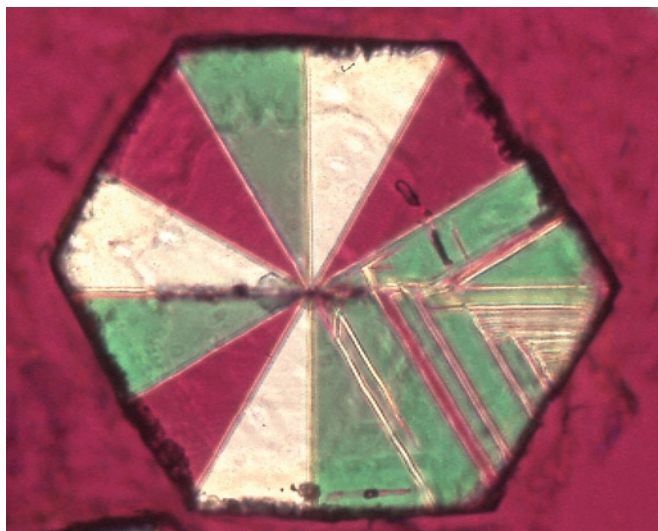


Figure 5. Photomicrograph of 2,10-undecanedione/urea (crossed polarizers, λ plate) grown in less than a minute by evaporation of methanol. The horizontal dimension of the crystal is 65 μm . Differently oriented domains, which are separated by the twin boundaries shown in Figure 4, are distinguished by their interference colors. For example, the beige and green sectors at the bottom of the crystal are separated by the (130)(130) interface shown in Figure 4a.

establish the direction of the slow axis. For larger retardations, it is possible to establish the absolute retardation (i.e. the order) by collecting intensity data at three wavelengths.⁵ In the example shown below the crystal was thin enough for one wavelength to yield the correct indicatrix orientation.

For ferroelastic crystals such as 2,10-undecanedione/urea, the orientation map reveals domain orientations directly since the slow axis corresponds to [100]. The retardation map contains further information about disorder within and between domains and can be used to identify the most highly ordered regions of a sample for crystallographic structure analysis. With in situ stress experiments, domain switching can be imaged directly and hysteresis loops can be generated. This method is therefore an important complement to our in situ stress studies using synchrotron white beam X-ray topography, which can be used to evaluate dislocations and strain in the presence and absence of stress.

For crystals containing an 80:20 mixture of 2,10-undecanedione and 2-undecanone, the ferroelastic domain switching is reversible, and the crystals display remarkable memory effects in which the daughter formed under stress quickly reverts to the original orientation when the stress is released. The memory effects are thought to be related to differences in perfection between the mother and daughter domains, so the retardation map, which provides information about perfection, is useful for evaluating these differences (Figure 6).

The Metripol microscope is especially useful for ferroelastic crystals in which the distortion from hexagonal metric symmetry is small (or zero with optically anomalous crystals). In such crystals, the birefringence is typically so small that ordinary light microscope techniques cannot be used to distinguish different sector orientations. In ferroelastic crystals of 2,19-eicosanedione/urea, for example, birefringence mapping reveals domain orientations quite readily. Because the distortion from hexagonal metric symmetry is so small in this crystal, ordinary rules of epitaxy do not apply, and domains that would ordinarily be mismatched can coexist on either side of a common domain wall.

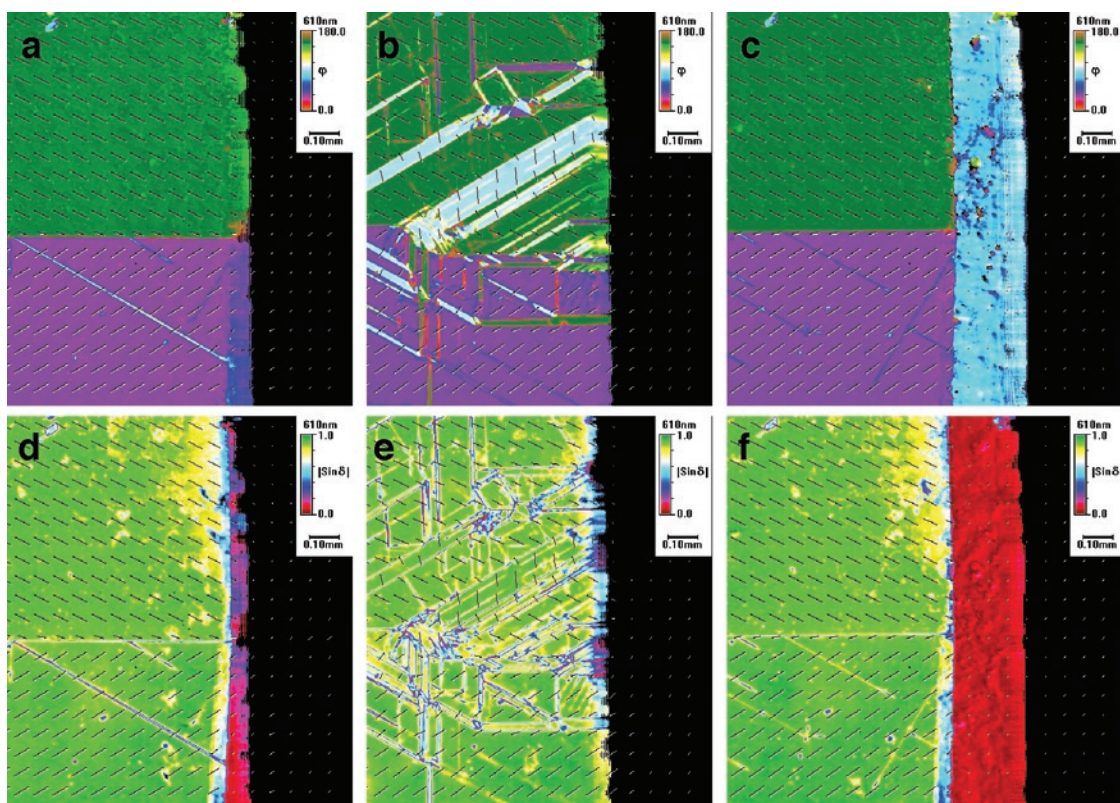


Figure 6. Metripol images ($\lambda = 610$ nm) of a portion of a urea inclusion crystal containing an 80:20 mixture of 2,10-undecanedione and 2-undecanone. The top panel (a-c) shows orientation maps for the crystal before stress (a), under 21 centiNewtons of force applied horizontally across the face (b), and after release of stress (c). The bottom panel (d-f) contains the retardation images for the same conditions as a-c. In each image, the color scale shows either the orientation of the slow axis (top panel) or the retardation as $|\sin \delta|$ (bottom panel), and the lines depict the orientation of the slow axis and the magnitude of the retardation. This crystal contains a horizontal (130) twin boundary, as depicted in Figure 4. In figure b, the slow axis of the daughter domain (light blue) is vertical. This corresponds to the [100] axis, as depicted in Figure 1. The changes in retardation shown in e (and which are related to crystal perfection) are not easily discerned with ordinary light microscopy.

Because the birefringence maps generated by the Metripol can take as little as a few seconds to generate, this method should be useful for *in situ* monitoring of crystal perfection during growth. In our work, it is rapidly becoming an indispensable tool for studying ferroelastic and ferroelectric domain switching and mechanisms of crystal growth.

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KINETIC MONTE CARLO SIMULATIONS OF ROD EUTECTICS AND THE SURFACE ROUGHENING TRANSITION IN BINARY ALLOYS

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Abstract

In this paper we report on two related topics: Kinetic Monte Carlo simulations of the steady state growth of rod eutectics from the melt, and a study of the surface roughness of binary alloys.

We have implemented a three dimensional kinetic Monte Carlo (kMC) simulation with diffusion by pair exchange only in the liquid phase. Entropies of fusion are first chosen to fit the surface roughness of the pure materials, and the bond energies are derived from the equilibrium phase diagram, by treating the solid and liquid as regular and ideal solutions respectively. A simple cubic lattice oriented in the $\{100\}$ direction is used. Growth of the rods is initiated from columns of pure B material embedded in an A matrix, arranged in a close packed array with semi-periodic boundary conditions. The simulation cells typically have dimensions of 50 by 87 by 200 unit cells. Steady state growth is compliant with the Jackson-Hunt model. In the kMC simulations, using the spin-one Ising model, growth of each phase is faceted or non-faceted phases depending on the entropy of fusion.

There have been many studies of the surface roughening transition in single component systems, but none for binary alloy systems. The location of the surface roughening transition for the phases of a eutectic alloy determines whether the eutectic morphology will be regular or irregular. We have conducted a study of surface roughness on the spin-one Ising Model with diffusion using kMC. The surface roughness was found to scale with the melting temperature of the alloy as given by the liquidus line on the equilibrium phase diagram. The density of missing lateral bonds at the surface was used as a measure of surface roughness.

Introduction

The goal of this project is to gain insight into the kinetics of growth in faceted / non-faceted rod eutectic (irregular eutectic) alloys. These eutectic alloys often form irregular microstructures. For example, controlling the microstructure uniformity in irregular eutectics such as Ge-TiGe₂ and Si-TaSi₂ is critical in controlling their structural and electronic properties. Regular eutectics, where both phases are non-faceted, closely follow the Jackson-Hunt model,^{1,2} whereas irregular eutectics usually grow with a larger inter-phase spacing than predicted. This behavior is highlighted with the discrepancies reported between ground based and micro-gravity measurements.^{3,4}

Irregular eutectics have previously been modeled using adaptations of the Jackson-Hunt model⁵⁻⁷, however these analytical models do not address the nucleation of new atomic layers on the faceted phase. We have conducted kinetic Monte Carlo simulations (kMC) of eutectic growth based on the spin-one

Keywords: rod eutectics, eutectic growth, kinetic Monte Carlo, surface roughing, spin-one Ising model, theoretical

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Ising model, which provides a definitive description of the solid-liquid interface above and below the surface roughening transition⁸. This model will be used to gain insight into the growth kinetics of systems comprised of both faceted and non-faceted solid phases.

The second part of this report examines the interface roughness of a binary alloy. Since regular and irregular eutectics are classified by the surface roughness of the solid phases, understanding the surface roughening behavior is important. The location of the surface roughening transition for the two phases of a eutectic alloy determines whether the eutectic morphology will be regular or irregular. Below the roughening transition, there is nucleation barrier to the formation of new layers exists, and the growth rate depends on the kink site density.^{9,10} As a result, the undercooling required for growth on smooth interfaces below the transition point is much greater than for interfaces above the surface roughening transition, so the two behave quite differently.

Kinetic Monte Carlo

Simulations for this study were conducted using a spin-one Ising model with the liquid assumed to be an ideal solution in contact with a regular solution solid, where both phases are comprised of A and B atoms. Simulations are implemented on an initially flat solid-liquid interface. Solid atoms are added to the solid from the liquid at a rate of:

$$v_i^{LS} = v_o \exp\left(\frac{\Delta S_i}{k_B}\right) \quad (1)$$

Here ΔS_i is the entropy difference between the liquid and the solid phases of the A and B atoms, v_o is the pre-exponential factor with units of 1/time, and k_B is the Boltzmann's constant. Correspondingly, atoms leave the solid and join the liquid at a rate of:

$$v_i^{SL} = v_o \exp\left(-\sum_j \frac{\Phi_{ij}}{k_B T}\right) \quad (2)$$

Here Φ_{ij} represents A-A, B-B, and A-B bonds in the solid and T is the temperature of the system. Both solid-liquid bonds and liquid-liquid bonds energies are set to zero. Simulations reported for this study are all done isothermally. The number of both A and B atoms was conserved in the simulation cell. Diffusion was conducted only in the liquid and was implemented by pair exchange of B atoms at a rate proportional to add-atom arrival.

$$v_i^D = \vartheta v_i^{LS} = \frac{6D}{a} \quad (3)$$

where ϑ is the proportionality constant. This rate may also be written in terms of the diffusion coefficient D and the cube root of the atomic volume a .

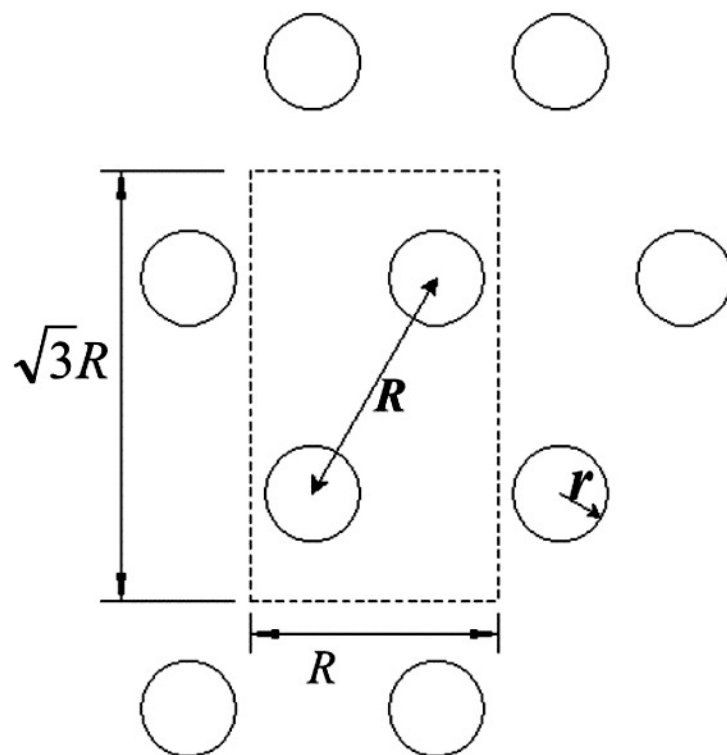


Figure 1. Simulation cell geometry.

Rods of solid B atoms are arranged in the simulation cell with semi-periodic boundary conditions in a closed packed formation. This is done with a simulation cell of R by $\sqrt{3} R$ where R is the rod spacing. The rod radius r is dependent on the eutectic composition.

These kMC simulations were implemented in a similar fashion to previous work,¹¹ events were chosen one at a time from a list of all possible events. The probability of choosing an event was inversely proportional to the frequency of that event. After the event is implemented the list is updated.

Rod Eutectic Simulations

The kMC simulations of a rod eutectic system started with a simulation cell where a liquid of randomly distributed A and B atoms was in contact with a solid consisting of columns of pure B embedded in an A matrix. The rods were arranged in a close packed formation in the simulation cell with periodic boundary conditions normal to the growth direction, as displayed in figure 1. The rod positions and radii are not confined in the simulation cell, however the simulation cell does place an upper limit on the rod spacing. Thus, the size of the simulation cell is an important parameter in these simulations.

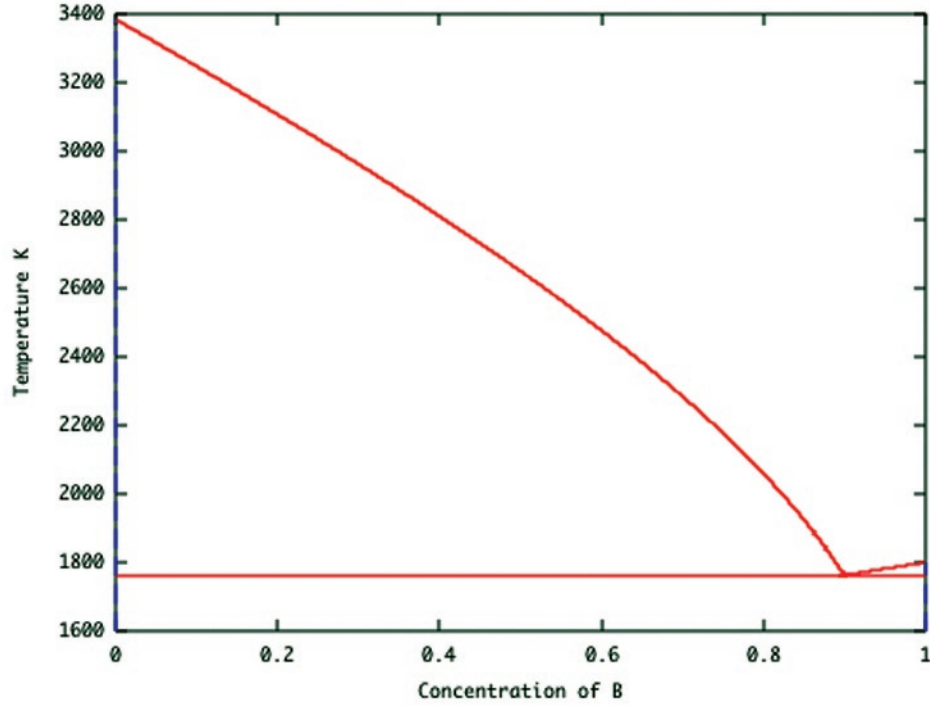


Figure 2. Sample phase diagram.

In the binary eutectic systems studied, the α and β phases contained very little of the second component.

The solidus lines in the phase diagram above are indistinguishable from the axis. This phase diagram was derived from the following bond energies:

$$\Phi_{AA} / k_B = 2820 \text{ }^\circ\text{K}, \Delta S_A = 2.5 k_B, \Phi_{BB} / k_B = 3000 \text{ }^\circ\text{K}, \Delta S_B = 5.0 k_B, \Phi_{AB} / k_B = 500 \text{ }^\circ\text{K}$$

Phase Diagram

Equilibrium phase diagrams for our eutectic systems were calculated for an ideal liquid in contact with a regular solution solid. In order to examine rod eutectic systems we used phase diagrams where the eutectic composition of the minor component was at 10%. The α and β phases in the eutectic systems used in this study contained very little of the second component.

Jackson-Hunt model

Starting values for the rod spacing R , which depends on the diffusion coefficient D and the simulation temperature, were derived from the Jackson-Hunt modeled. The temperature of the simulation, $T = T_E - \Delta T$, was chosen for reasonable rod spacing:

$$\Delta T \cdot R = C_1 (\Phi_{ij}, T_E, C_E, m_\alpha, m_\beta) \quad (4)$$

Where T_E and C_E are the eutectic temperature and composition and m_α and m_β are the slopes of the liquidus lines of the α and β phases at the eutectic point. Rod spacing R of ~ 90 unit cells were chosen based on computational restraints.

The rod spacing is related to the diffusion coefficient (D) by:

$$R^2 \cdot D = C_2 (T_E, C_E, \Delta S_\beta) \quad (5)$$

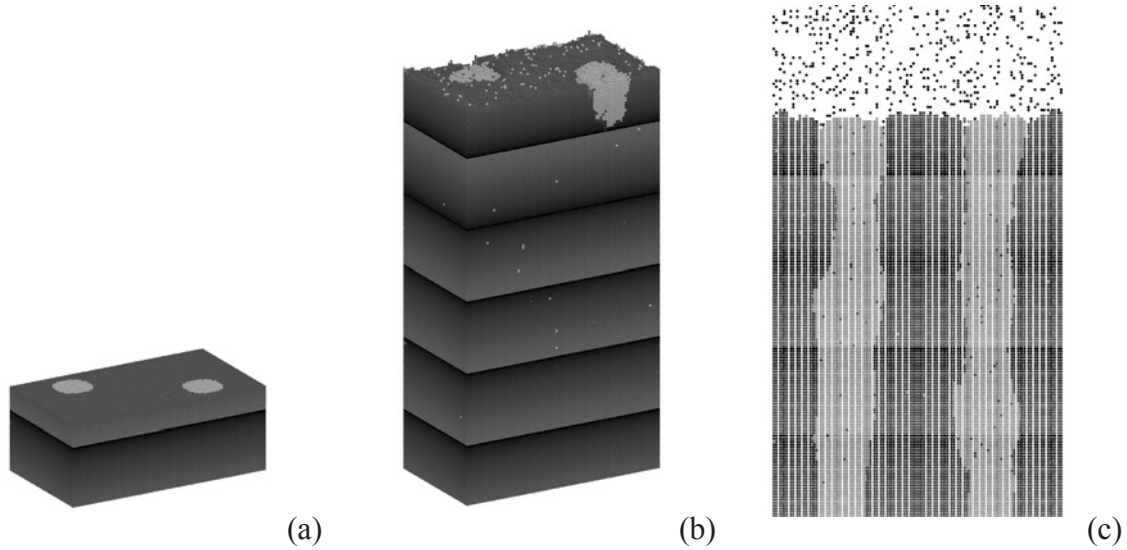


Figure 3. Typical simulation results.

(a) and (b) are 3D perspective views of the solid atoms in the simulation cell. (c) is a diagonal slice through the simulation cell of figure (b) where A and B solid atoms and B liquid atoms are displayed.

The simulations cell has dimensions of 50 by 87 by 230 unit-cells. Figures were rendered using Raster3D.¹²

$$\Phi_{AA} / k_B = 2820 \text{ }^\circ\text{K}, \Delta S_A = 2.5 k_B, \Phi_{BB} / k_B = 3000 \text{ }^\circ\text{K}, \Delta S_B = 5.0 k_B, \Phi_{AB} / k_B = 500 \text{ }^\circ\text{K}$$

$$T_E = 1762.6 \text{ }^\circ\text{K}, \Delta T = 68 \text{ }^\circ\text{K}$$

Results

Simulations of stable growing rod eutectics were based on a simple cubic lattice oriented in the $\{100\}$ growth direction. Stable rod growth was achieved when the liquid was 3% richer in the minor component as compared to the equilibrium phase diagram. The rods were also observed to modulate in thickness when the liquid was off this composition. Both of these behaviors are experimentally observed characteristics. An example of one of these simulations is displayed in figure 3.

Irregular Eutectics

Interest in examining the roughening behavior of the binary alloy was motivated by the simulation above. With a simple cubic simulation cell oriented in the $\{111\}$ direction and both A and B atoms having the same ΔS 's, we observed the surface roughness of the two phases was clearly different. The minor phase clearly showed faceting while the interface of the major phase was rough. We also observed that it was more difficult to get stable growth of faceted rods if the facets were in the plane of the growth direction. At this point we changed our focus from SC to FCC lattices since the SC $\{111\}$ simulations cell does not tessellate in the same way as the SC $\{100\}$ simulation cell. Since FCC $\{111\}$ planes have more in the plane nearest neighbors than $\{100\}$ direction systems may be rough $\{100\}$ faces while facets in the $\{111\}$ direction.

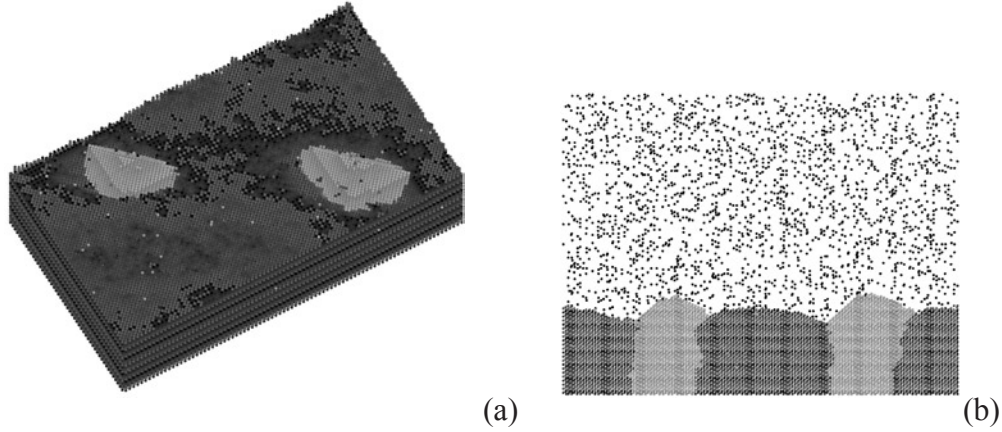


Figure 4. Irregular rod eutectic.

Simulation conducted on a simple cubic lattice oriented in the $\{111\}$ growth direction. Both A and B atoms gave the same ΔS however the surface roughness characteristics of both the alpha and beta phase are clearly different. Faceting is along of the $\{100\}$ faces. The 3D perspective view of figure (a) is distorted into a rectangular simulation cell. Figure (c) is a diagonal slice through the simulation cell.

$$\Phi_{AA} / k_B = 2000 \text{ }^\circ\text{K}, \Delta S_A = 5.0 k_B, \Phi_{BB} / k_B = 1650 \text{ }^\circ\text{K}, \Delta S_B = 5.0 k_B, \Phi_{AB} / k_B = 300 \text{ }^\circ\text{K}$$

$$T_E = 1028.2 \text{ }^\circ\text{K}, \Delta T = 9.2 \text{ }^\circ\text{K}$$

Surface Roughness

While the surface roughening transition of single component systems has been studied,¹³⁻¹⁵ the surface roughening transition for binary systems has not. We have conducted a study of the inter-facial roughness in alloys using the spin-one Ising Model with diffusion using kMC to understand the roughening behavior of the individual phases in the rod eutectic system. We have found that the surface roughness depends on the bond energies and melting temperature as given by the liquidus temperature on the equilibrium phase diagram.

The surface roughness can be defined in terms of the density of lateral bonds missing at the surface. In this study, the definition of surface roughness which was used is the same as used in BCF¹⁶:

$$s(t) = \frac{N_{SL}(t) - N_{SL}(0)}{N_{SL}(0)} \quad (6)$$

Here $N_{SL}(t)$ is the number of solid-liquid bonds on the surface and $N_{SL}(0)$ is the number of solid-liquid bonds on an atomically smooth surface. This does not define the location of the surface roughening transition, since the surface roughness increases smoothly through the transition. However, the location of the surface roughening transition can be determined from height-height correlations in the configurations of the interface.

For melt growth of single component materials, the location of the surface roughening transition is given by the Jackson α -factor.

$$\alpha = \left(\frac{L}{k_B T_m} \right) \left(\frac{\eta}{Z} \right) \quad (7)$$

Here L is the latent heat of fusion, T_m is the melting temperature of the system, η is the number of bonds in the plane of the interface, and Z is the coordination number of the lattice.

Surface Roughness Simulations

The relationship between surface roughness and the α -factor was examined on a FCC lattice oriented in the $\{100\}$ direction. Simulation cells typically had dimensions of 200 by 200 by 100 unit cells. Solid-liquid interfaces were created flat with pure solid of A atoms and a mixture of A and B atoms in the liquid. The evolution of structure of the interface then proceeded at the liquidus temperature of the binary alloy.

Surface Roughness Results

Three separate phase diagrams using different entropies of fusion for the pure α phase were used in the simulations reported here. System 1 was run with a ΔS of $7.0 k_B$, system 2 with a ΔS of $6.0 k_B$ and system 3 with a ΔS of $5.0 k_B$. Pure systems were also simulated over a similar range of α -factor values. Surface roughness as a function of α -factor values is reported in figure 5. Rather than using the melting point of the pure material to calculate the α -factor for the alloys, the liquidus temperature of the binary systems was used. Error bars on the data are the standard deviation of the fluctuations of the roughness value around the reported mean. Different α -factors values apply for each point along the liquidus lines of each phase diagram. From figure 5 it is evident that both pure and binary systems follow the same roughness relationship with a smooth monotonically decreasing roughness with increasing α -factor.

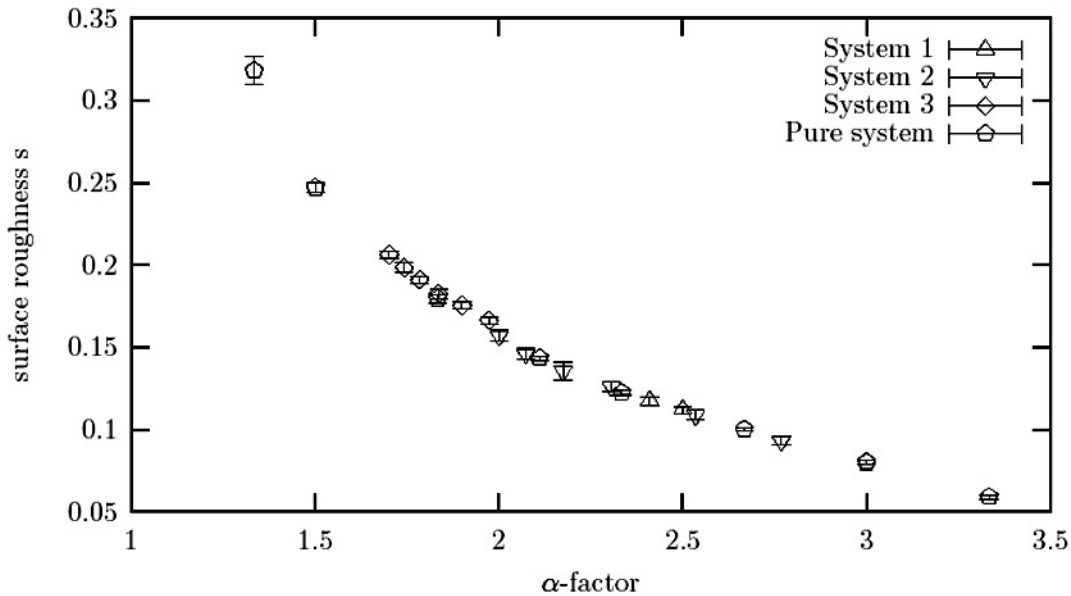


Figure 5. α -factor vs. roughness parameter

Both binary and pure systems follow the same roughness relationship

System 1: $\Delta S_{\text{both}} = 7.0 k_B$, $\Phi_{AA} = 1500^\circ K$, $\Phi_{BB} = 2000^\circ K$, $\Phi_{AB} = 500^\circ K$
System 2: $\Delta S_{\text{both}} = 6.0 k_B$, $\Phi_{AA} = 1470^\circ K$, $\Phi_{BB} = 2000^\circ K$, $\Phi_{AB} = 500^\circ K$
System 3: $\Delta S_{\text{both}} = 5.0 k_B$, $\Phi_{AA} = 1310^\circ K$, $\Phi_{BB} = 1800^\circ K$, $\Phi_{AB} = 500^\circ K$

In the case of this simple eutectic system the surface roughness of both phases increases as the system moves to either side of the eutectic. In a rod eutectic system this is more dramatic for the minor phase because of the larger difference between the melting temperature of the pure material and the alloy.

Conclusions

We have developed and demonstrated a kMC spin one Ising model capable of simulating the growth of stable rod eutectics. The simulations use the Jackson-Hunt model as a guide to provide appropriate starting conditions. These simulations exhibit behaviors similar to experimentally observed eutectic structures. While irregular rod eutectic growth has been more challenging, simulations where the minor phase is faceted have been more successful when the faceted interface has been out of the plane of the growth direction. Since the surface roughness of the two solid phases plays an important role in the development of the microstructure, an investigation of the surface roughness of binary alloys was conducted. It was found that the surface roughness of alloys follows the same behavior as pure materials provide that the liquidus temperature is used to calculate the α -factor. The entropy difference between pure solid and pure liquid of the same material is not the same as the entropy difference between the solid and the liquid alloy, and this difference is expressed in terms of the lowered melting point. The surface roughening of a phase in a eutectic alloy does not depend on the entropy of fusion of the pure components: the interfaces of the alloy are smoother than the interfaces of the pure materials.

Acknowledgments

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DIFFERENT RULE SETS FOR CELLULAR AUTOMATA MODELING OF PERITECTIC DENDRITIC GROWTH

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Introduction

Peritectic alloys display a wide variety of growth morphologies from coarse dendritic microstructures to finer two-phase microstructures suggesting coupled growth. Lee and Verhoeven¹ noted that a finely spaced cellular-like microstructure formed during directional solidification of a peritectic Ni-Ni₃Al alloy. For large G/V growth conditions, the familiar banded microstructure formed. However, at moderate G/V conditions (but still in the range for planar growth as originally defined by Boettinger²), a type of coupled growth occurred. This structure consisted of cells of Ni₃Al surrounded by a Ni solid solution, with the growth front terminating at a sharp isothermal interface. Lee and Verhoeven termed this microstructure “cellular coupled growth.” Another example of coupled growth has been reported by Li et al³ for a Zn-rich Zn-Cu alloys. Here, the resultant microstructure consisted of primary dendrites of CuZn₅ and a lamellar matrix consisting of CuZn₅ and solid-solution Zn.

The primary goal of our research is to explain the morphological development of two-phase peritectic alloys by coupled experimental and numerical procedures. Towards this end, the present paper reports the development of a cellular automaton (CA) model that will be used to predict the growth morphology of peritectic alloys. The preliminary model considers only dendritic growth of the primary phase as governed by a physically realistic set of rules. This paper will describe the development of those rules. The current model will serve as a building block for further work on two-phase peritectic solidification. The Zn-rich Zn-Cu alloys were chosen for the numerical simulations as Ma et al.⁴ have recently developed a solidification microstructure selection map for these peritectic alloys.

Modeling of dendrites by CA technique has been carried out by many investigators^{5,6,7}. Brown and Spittle⁵ modeled the growth using special rules to represent the heat transport, curvature and liquid-solid transformation. Diltney and Pavlik⁶ modeled the growth considering the effects of curvature and anisotropic surface tension. They modeled the growth of dendrites under different processing conditions and qualitatively compared the results to experiments.

The present two dimensional model simulates dendritic growth by allowing a planar solid-liquid interface to break into cells and dendrites due the presence of constitutional supercooling. Morphological instabilities are due solely to solutal effects. The stabilizing effects of surface tension and curvature at the solid-liquid interface are also considered. Different sets of growth rules are examined for their ability to grow qualitatively reasonable results.

Keywords: peritectic solidification, cellular automata, theoretical

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Model Development

The task of modeling these transient microstructures is performed using a combination of techniques. A growth model that uses modified cellular automata techniques to determine the progression of the solid front and local redistribution of solute is linked to the solution of the mass transport equation.

Growth Model

Cellular automata (CA) are mathematical models of physical systems in which time, space, and dependent variables have been discretized, that is, they are modeled as taking only a finite set of discrete values. The model is solved by stepping through time and examining the state of the variables at each of these discrete locations in space. The new state at each location (or cell) is determined by the current states of neighboring locations and all locations are updated simultaneously. (In this work, the usual practice is changed by not updating all of the cells simultaneously. Due to numerical stability considerations related to solute rejection during solidification, liquid cells are picked in random order, subjected to the transition rules and updated immediately.) In order to model microstructural development of metal alloys using CAs, the first step is to list the attributes of the CA: cell geometry and definition of cell neighborhood, number and types of cell states, and transition rules governing cell state and its changes⁸.



Figure 1: Two-dimensional arrays of CA cells showing different neighborhoods:
(a) 8 cell neighborhood (b) 4-cell neighborhood.

The cell geometry is laid out first, by superimposing a grid on the domain of interest. It is possible to use a hexagonal array of cells, but in this study the cells are placed in a uniform two dimensional Cartesian grid. Figure 1 shows two different neighborhood definitions: first and second nearest neighbors (Figure 1(a)) and first nearest neighbors (Figure 1(b)). The neighborhood of a cell is important because it is the only region that has an influence on the new state of the cell at a particular time. The cells in the CA grid will either be in the solid or a liquid state and the transition rules that determine the current and new state of a cell are described below.

For a given cell to be transformed from liquid to solid, certain conditions must hold in that cell. First, the composition of the liquid must be under the liquidus line of the alloy (C_L^*):

$$C_L^* = C_o - \frac{(T_{Liq,o} - T)}{m_L}, \quad (1)$$

where $T_{Liq,o}$ is the liquidus temperature of the alloy at the initial composition (C_o), T is the local temperature and m_L is the slope of the liquidus line. This equation for the liquidus composition as a function of temperature assumes no curvature undercooling, which will be added in the third rule set. Another rule is that a liquid can freeze only if there are a minimum number of solid neighbors around it (the number and neighborhood are different for each set of rules defined below). In all cases studied here, solid exists at the beginning of the simulation and no nucleation events take place.

The first rule set (Set #1) requires two adjacent cells in the 8 cell neighborhood to be solid for a liquid cell to change to solid. For reasons discussed in the results section, this number was changed to three adjacent cells in Set #2.

The third rule set includes the effect of the curvature of the surface influencing the local liquidus temperatures. The surface tension of the liquid-solid interface tends to suppress any instabilities in the surface and hence introduces an undercooling on the liquidus temperature. Equation (1) is modified to account for this downward shift in the liquidus line (ΔT_c) caused by increased curvature of the solid:

$$C_L^* = C_o - \frac{(T_{Liq,o} - T - \Delta T_c)}{m_L}. \quad (2)$$

The undercooling due to curvature is:

$$\Delta T_c = -\frac{\sigma}{S_m} \kappa, \quad (3)$$

where σ_o is the surface tension, S_m is the entropy of melting, and κ is the curvature of the solid-liquid interface.

The dendrites grow in a preferred growth orientation based on the crystal structure of the solid phase formed. A cubic crystal would grow most rapidly in $\langle 100 \rangle$ directions. The solid phase was assumed to have a cubic crystal structure in the current model. The surface tension as a function of the relationship between the surface normal and the preferred growth direction is:

$$\sigma_\theta = \sigma_o(1 + \delta \cos(4\theta)) \quad (4)$$

The angle θ is between the normal to the surface and preferred growth direction (Figure 2).

The surface tension in equation (4) is given as⁷:

$$\sigma = \sigma_\theta + \sigma_\theta''. \quad (5)$$

In the above equation, δ is the amplitude of variation of surface tension with θ . A value of δ was chosen to be 0.5, and a value of σ/S_m was chosen to be 1.9×10^{-7} mK in the current model.

To calculate the curvature of an interface, a circle of 3.5 cells radius is drawn from the cell of interest (the cell with a cross in Figure 2) and the area of solid inside the circle (N_s) is calculated⁷. The expression for curvature (κ) is given in equation (6).

$$\kappa = \frac{2.0 * (N_o - N_s)}{N_t * \Delta x} \quad (6)$$

N_o is the half area of the circle, N_t is the total area of the circle and Δx is the cell dimension.

Set #3 of the CA rules includes this curvature undercooling, but also changes the rule concerning number of neighbors necessary to grow solid. In this rule set, only one neighbor is necessary for growth, but it must be one of the nearest neighbors (in the 4 cell region in Figure 1(b)), allowing more freedom to grow at any desired angle compared to Set #2. To restrain the growth somewhat, an additional rule that N_s has to be greater than 15% of the circle area was incorporated. This is a physically realistic assumption which prevents growth from occurring if the tip radius is smaller than the critical radius of nucleation.

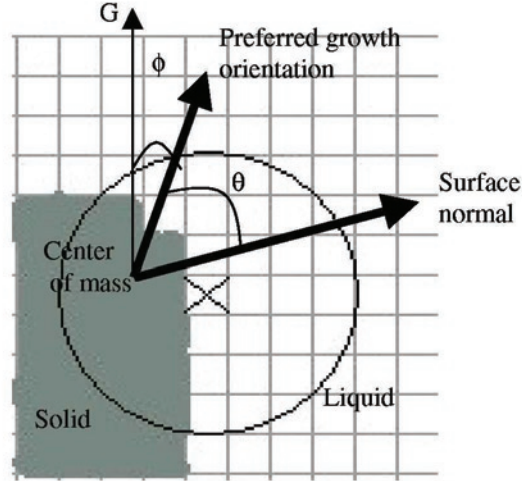


Figure 2: Schematic diagram showing important directions and the region used to determine surface normal.

Solute Transport Model

The growth of the solid is governed by the rules listed above, which are directly influenced by the local composition in the liquid. Upon solidification, the alloy partitions according to the phase diagram and new solid takes the composition determined by the solidus line at the local temperature. Any solute remaining is rejected into all of the surrounding liquid cells. (Similarly, if the solid is richer in solute than the liquid, solute is absorbed from all of the surrounding liquid cells.) This partitioning sets up composition gradients in the liquid and solid and the consequent diffusion must be modeled to predict microstructural development.

The composition distributions in the domain were calculated from the conservation equation for solute:

$$\frac{\partial C}{\partial t} = D_m \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) \quad (7)$$

An implicit finite volume method was used to solve for the transient diffusion in equation (7)⁹. The uniformly square cells of the CA method corresponded to the control volumes for the FV calculations. The boundaries of the computational domain were made impermeable. The mean diffusion coefficient, D_m , was found using a harmonic mean, which accurately represents the diffusion across volume interfaces⁹. The growth model and the solute transport model are solved sequentially in each time step without iterating between the two.

Numerical Cases

Seven cases were run using the model described above. The differences among these cases are seen in Table 1 and the choice of these rule sets will be discussed in detail in the next section. In all the simulations, a plane front of solid filling the row of cells at the lowest temperature was allowed to grow. A uniform temperature gradient G was imposed on the domain and this gradient was moved with velocity V . The gradient for all of these cases was 10 K/mm and the velocities varied as shown in Table 1. The cell (control volume) size was 5 μm and the time step was 0.001 seconds.

Table 1. Operating conditions for different cases.

Case	velocity (m/s)	CA rule set	Curvature effects	Comments
1	1×10^{-4}	1	absent	
2	5×10^{-4}	1	absent	
3	1.67×10^{-4}	2	absent	
4	1.67×10^{-4}	2	absent	G at 45° from y-axis
5	1.67×10^{-4}	3	present	$\phi = 30^\circ$ from G
6	1.67×10^{-4}	3	present	$\phi = 45^\circ$ from G
7	1.67×10^{-4}	3	present	$\phi = 0^\circ$ from G

The simulations were done for a Zn-Cu5wt% alloy, the phase diagram of the alloy of which is shown in Figure 3. This alloy has a partition coefficient of 3.0 and, the slope of liquidus line (m_L) is $20.0^\circ\text{C}/\text{wt}\%$. The diffusion coefficient of solute in liquid (D_L) is $10^{-8} \text{ m}^2/\text{s}$, and the diffusion coefficient in solid (D_S) is $2 \times 10^{-12} \text{ m}^2/\text{s}$.

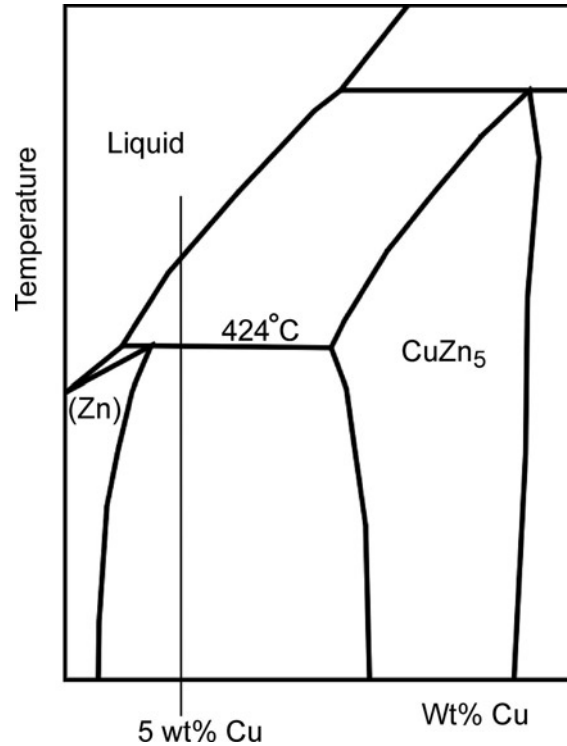


Figure 3: Schematic of the Zn-Cu phase diagram.

Results and Discussion

The results from cases number 1 and 2 (Table 1) are shown in Figure 4. A dendritic pattern is clearly obtained. Furthermore the primary and secondary arm spacing decreases with increasing velocity as expected (Figures 4(b)&(c)). However, a strong grid dependence is found as growth is oriented 45° degrees to the imposed thermal gradient. As no crystallographic effects have been incorporated in the rule set (Set #1), the preferred growth is related to the way in which solute is redistributed. This problem is illustrated in Figure 5 where the center cell (which has just solidified) has two solid neighbors in an 8 cell region, thus satisfying one of the requirements of Set #1. However the liquid cell labeled as 2 will have more solute than cell 1. This is simply because cell 2 has fewer solid neighbors that have rejected solute

into it. Therefore, cell 2 will have the higher probability to solidify next. As solidification proceeds, this pattern continues, resulting in the grid dependent morphology shown in Figure 4.

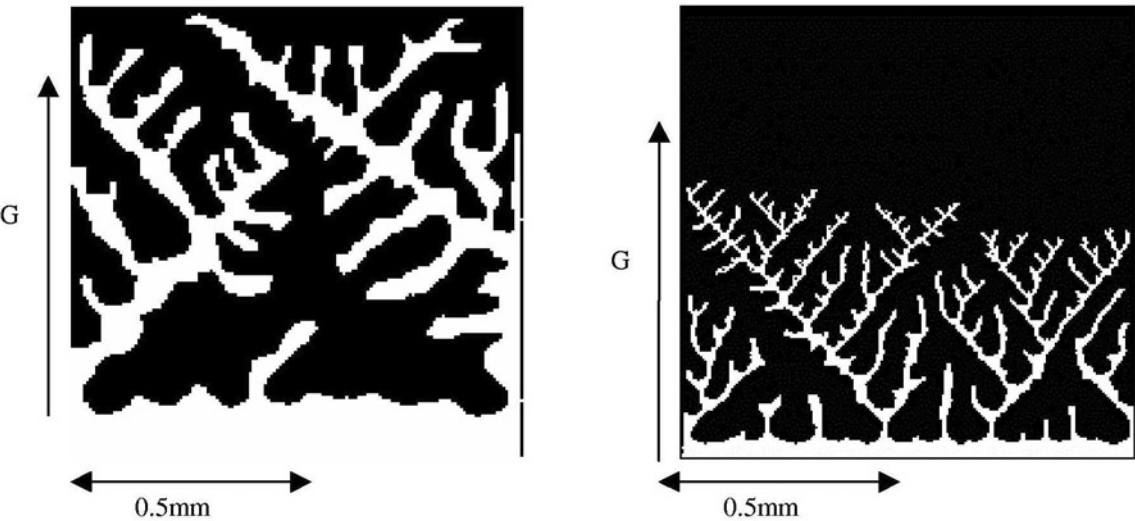


Figure 4: Numerical results at 35 s showing the grid dependence resulting from using Rule Set #1. (a) Case 1. (b) Case 2.

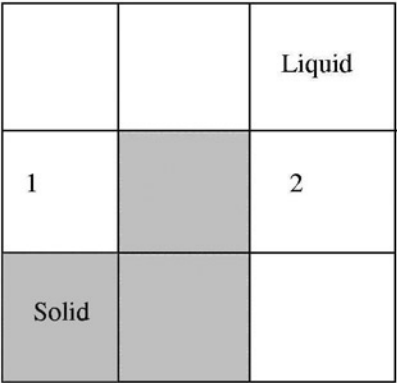


Figure 5: Schematic showing the unsymmetrical solute redistribution of Rule Set #1.

To reduce the grid dependence, a set of rules allowing for a symmetrical redistribution of solute is needed. This redistribution can be achieved by requiring 3 solid nearest neighbors as defined in Set #2. A schematic showing the way in which solute redistributed using Set #2 is shown in Figure 6. Here, both liquid cells 1 and 2 have equal probability to solidify.

Using Rule Set #2, the results of cases 3 and 4 are shown in Figures 7(a)&(b). From these figures, the grid dependent growth is clearly reduced. In Figure 7(a) the thermal gradient is aligned with the vertical axis, while in Figure 7(b) the thermal gradient is maintained 45 degrees to the grid-axes. However, for both cases the primary dendritic growth is parallel to the thermal gradient as expected because crystallographic effects have not yet been incorporated into the model. Furthermore, because the operating conditions are the same for both cases 3 and 4, the same dendritic arm spacing and tip radius are found Figures 7(a)&(b).

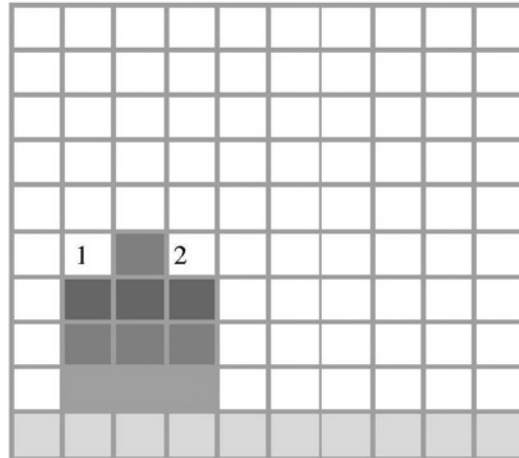


Figure 6: Schematic showing the symmetrical solute redistribution of Rule Set #2.

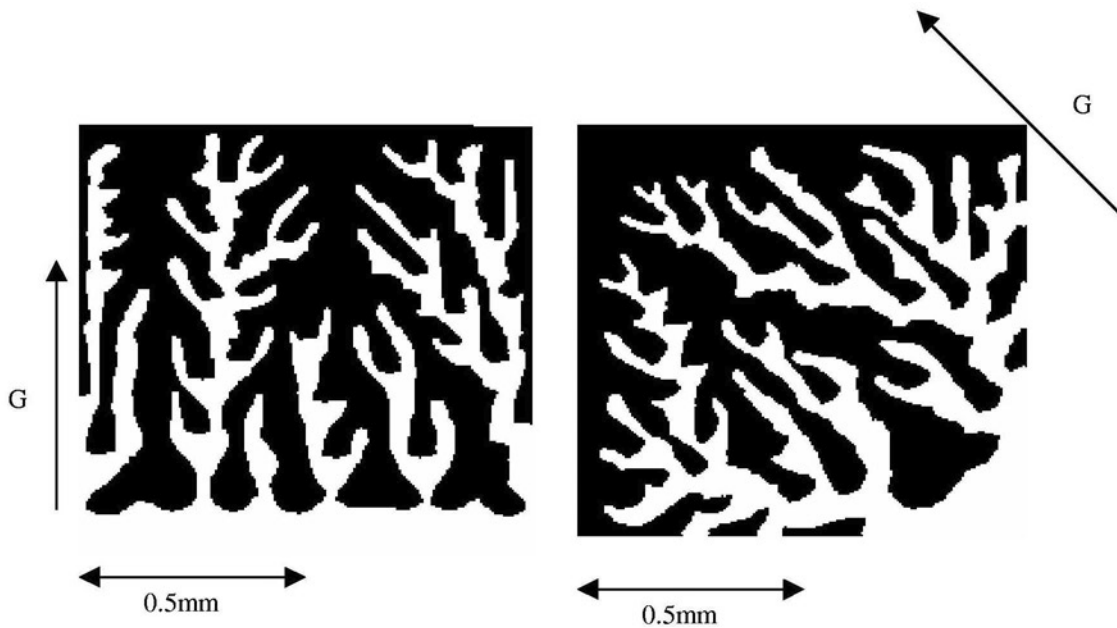


Figure 7: Numerical results at 35 s showing the reduced grid dependence from using Rule Set #2.
(a) Case 3. (b) Case 4.

The morphological instability producing the dendritic patterns shown in Figure 7 are due to solutal effects. Shown in Figure 8 is the concentration variation in the solid and liquid for Case 3. (Note that this snapshot is taken at an earlier time than that shown in Figure 7(a).)

The concentration profile ahead of the dendrite tip marked in Figure 8 with a box is shown in Figure 9(a), and the corresponding plot of the liquidus and imposed temperature gradient is shown in Figure 9(b). The liquid ahead of the dendrite tip is constitutionally supercooled. However, the large degree of supercooling indicated in Figure 9(b) suggests that the dendrite tip velocity is slower than that of the moving temperature field.

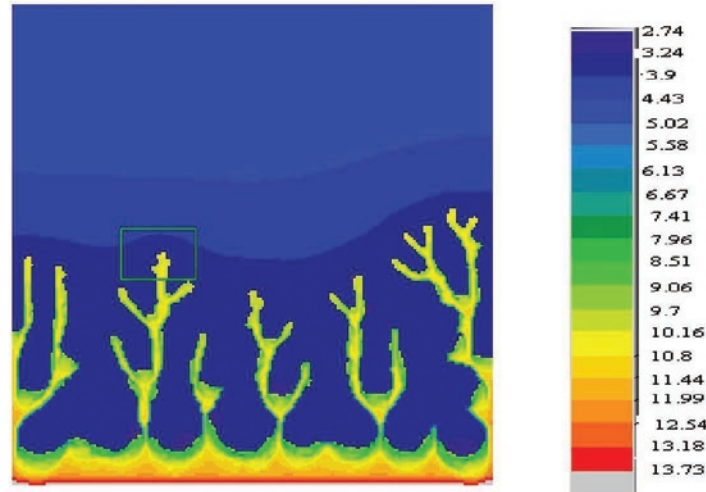


Figure 8: Solute concentration distribution in wt% Cu for Case-3.

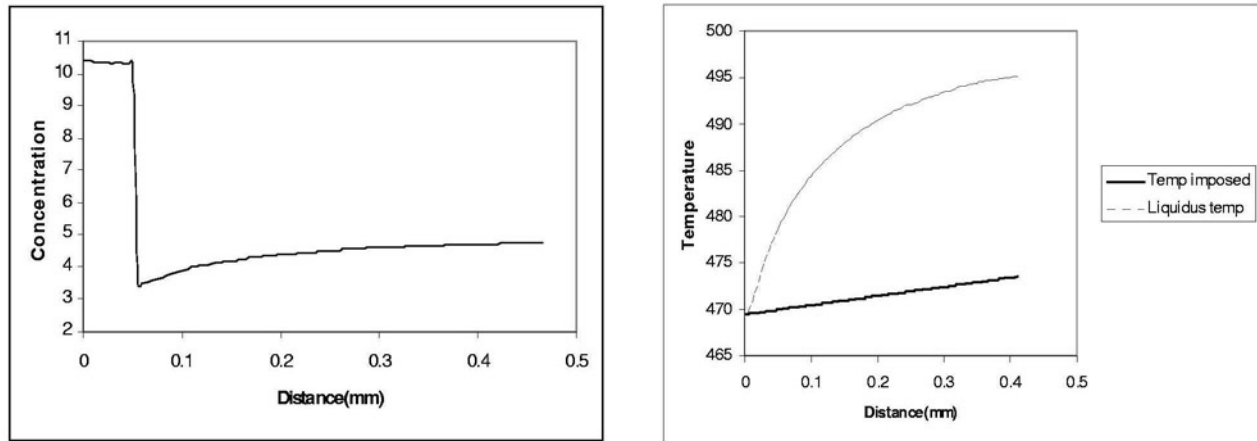


Figure 9: Concentration and temperature profiles in front of the dendrite tip in Figure 8.

The last results are those in which surface tension and curvature effects are included as defined by Rule Set #3. The results from cases 5, 6, and 7 in which the preferred growth direction is varied with respect to the imposed temperature gradient are seen in Figure 10.

The preferred dendritic growth directions of the microstructures shown in Figure 10 are controlled by the orientation of the initial solid (which originally had a planar morphology), and the preferred growth direction is not directly dependent on the numerical grid. However the dendritic arm spacings shown in Figure 9 are much coarser than actual experimental results. This may likely be due to the coarse grid spacing chosen for the numerical experiments. The present set of simulations were made mainly to explore how different rule sets would affect the dendritic growth morphology.

Conclusions

Three different rule sets were examined for modeling dendritic growth by CA techniques. The dendritic morphology is very sensitive to the method in which solute is redistributed in the Cartesian grid. Rule

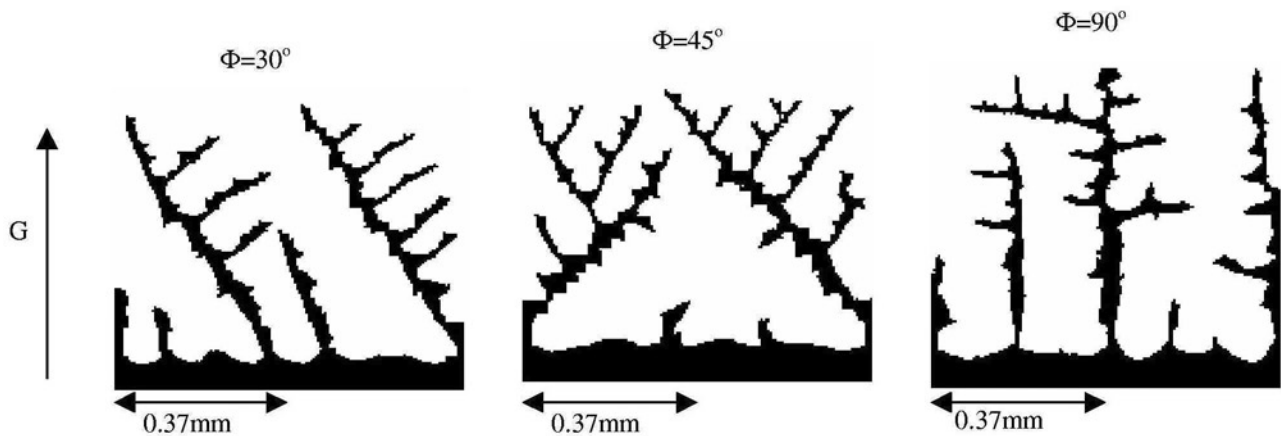


Figure 10: Numerical results after 18 s showing preferred crystallographic growth induced by Rule Set #3 for (a) Case 5, (b) Case 6, and (c) Case 7.

Set #1 resulted in an asymmetrical solute redistribution pattern resulting in strong grid dependent growth. Grid dependence was reduced by increasing the number of nearest neighbors needed in the rule set (Set #2) to provide for a symmetrical solute redistribution pattern. However, the increased number of nearest neighbors constrains the growth morphology to the Cartesian grid shape for the local neighborhood. Grid dependence was reduced further by estimating the curvature at the interface and including this information in the rule set. This was successfully accomplished with the third rule set (Set #3) in which only one nearest neighbor is required. Rule Set #3 also allows for inclusion of curvature undercooling in the model and provides a physically realistic set of rules which can be used simulate dendritic growth.

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STUDIES OF PROPERTIES OF UNDERCOOLED GLASS FORMING METALLIC ALLOYS

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Bulk metallic glass forming liquids are metal alloys which exhibit a high degree of resistance to nucleation and growth of crystals. Such alloys can be processed for laboratory time scales in the deeply undercooled liquid state. This has made studies of thermophysical properties of these liquids from the equilibrium melt down to the glass transition temperature of the undercooled melt. Of particular interest is the study viscosity and atomic diffusion in these glass forming liquids. These properties are of particular interest as they relate to fundamental theories [1-4] of the glass transition in liquids, (e.g. Beta-Relaxations, Mode-Coupling Theory, Liquid Fragility, etc.)

High Vacuum Electrostatic Levitation (HVESL) Processing offer a platform for study liquids under high vacuum, containerless, and quiescent conditions. Using a NASA supported ESL facility located at Caltech, we have developed a method for laser heating and melting of spherical liquid drops under high vacuum conditions using a newly developed high symmetry 4-beam tetrahedral laser heating system. The liquid drop is melted, stably positioned, and subsequently brought to chosen temperature under very near isothermal conditions. Using symmetric heating, a 3mm sphere can be maintained at 1000 K with total temperature variations of order or less than 0.1 K over the sphere. Under such conditions, both gravity driven and Marangoni convection within the liquid sphere can be minimized. Steady state convective flow velocities of microns per second and less can be achieved. The liquid thus exhibits “benchmark” levels of quiescence. The “near quiescence” of the liquid allows, for the first time, direct measurements of intrinsic atomic diffusion constants and impurity diffusion constants in the liquid without contamination of the data by convection. The diffusants are deposited from the gas phase onto the surface of the levitated liquid drop and allowed to diffuse into the sphere. Depth profiles of the diffusant in the sphere are captured by relatively rapid “quenching” the sample from the measurement temperature to ambient and are later analyzed to obtain diffusion constants for the molten alloys.

Under microgravity conditions, g-driven convection can be mitigated still further to yield “benchmark” atomic diffusion measurements in liquids which are essentially “free” of convective contamination effects. In addition to development of the HVESL platform with symmetric laser heating, the present project includes direct measurements and modeling of the temperature distributions in the liquid drop, modeling of Marangoni and g-driven convective flows, and comparison of models with experimental results for actual samples processed in the ground-based Caltech HVESL using symmetric heating. HVESL data on actual glass forming liquids has been obtained to determine time-temperature-processing windows for liquid diffusion studies in the shallow and deeply undercooled regimes of several glass forming alloys. Using a combination of experiments and modeling, we have established [5] a “processing parameter” matrix which demonstrates the “window of opportunity” in which convection-free atomic diffusion studies can be carried out. Fig. 1 shows the Caltech HVESL facility which is being developed and utilized in this project.

Keywords: alloys, glass formation, atomic diffusion, electrostatic levitator, flight

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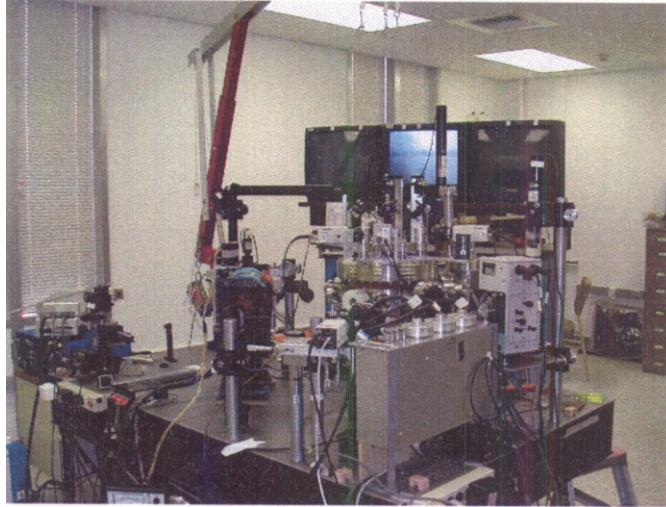


Fig.1 Caltech HVESL facility

Fig.2 shows a close-up view of the optical components that develop and implement high symmetry tetrahedral heating in the Caltech HVESL.

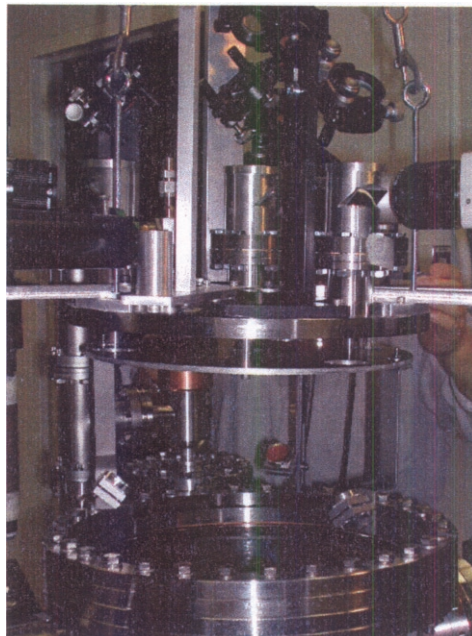


Fig.2 Tetrahedral Heating System on Caltech HVESL

To demonstrate the achievement of low temperature gradients in a molten liquid drop using the tetrahedral heating system, we have used ultra-fine (0.003") thermocouples arrayed on the surface of 302 Stainless Steel sphere of 10 mm diameter suspended on a quartz fiber in the HVESL. The sphere is heated with various laser beam geometries. Fig. 3 shows the maximum temperature variation on the sphere under heating by 4 tetrahedrally arranged laser beams in a focussed and spread condition. It can be seen that the latter configuration gives temperature variations of less than 1 K over the sphere surface.

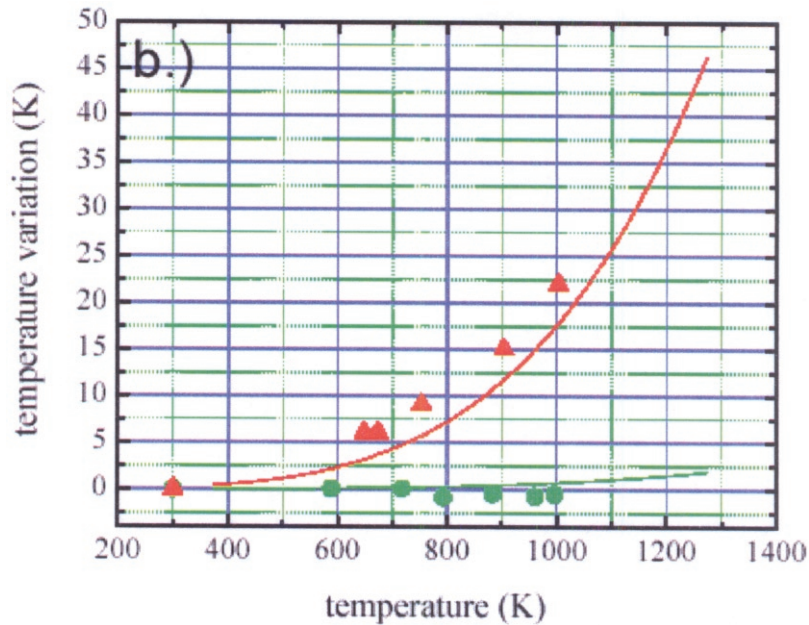


Fig. 3 Maximum measured temperature variation of 10mm stainless steel sphere. Red triangles - data with 4 “point” focused beams, Green circles - data with 4 “spread” laser beams. See ref. [5] for more details.

The window of opportunity for atomic diffusion experiments on a Zr-based glass forming alloy can be illustrated using process maps which show various time-temperature regimes for processing a deeply undercooled liquid [5]. The reader is referred to ref[5] for a more extensive discussion. Fig.4 shows an example of a “process map” for a Zr-Nb-NiCu-Al glass forming liquid. The dots are taken from HVESL data for the TTT-diagram for crystallization of the alloy on the HVESL[6]. The other shaded regions are “outside” the window for reasons indicated on the figure. For example, experiments conducted for too long a time lead to diffusion throughout the sphere and cannot be used to obtain useful atomic diffusion data. The “white” region is the window of opportunity for an atomic diffusion experiment under conditions which are free of convective contamination.

In summary, we have developed the Caltech HVESL as a platform for stable levitation and positioning of liquid alloy drops with sizes in the 2-3.5 mm range. Time-temperature-transformation diagrams have been experimentally determined for several bulk metallic glass forming alloys. These diagrams show the time available at a given undercooling during prior to the onset of crystallization. Using a tetrahedral 4-beam laser heating system in a “spread” beam geometry, we have established that temperature variations substantially less than 1 K can be achieved in the molten liquid drop. We have established that Marangoni and g-driven convection will be substantially reduced under such conditions. Specifically, convective flow velocities are reduced to the micron/s range. Under such conditions, one can carry out accurate measurements of the self-diffusion and chemical diffusion constants of various species in the molten glass forming liquids. Under microgravity conditions, we expect significant further reduction of convection by the mitigation of gravity. Based on this work, we have proposed a “benchmark” method for carrying out atomic diffusion measurements in reactive metallic liquids at elevated temperatures. The proposed flight experiment has completed a Science Concept Review and could be implemented given a suitable flight opportunity.

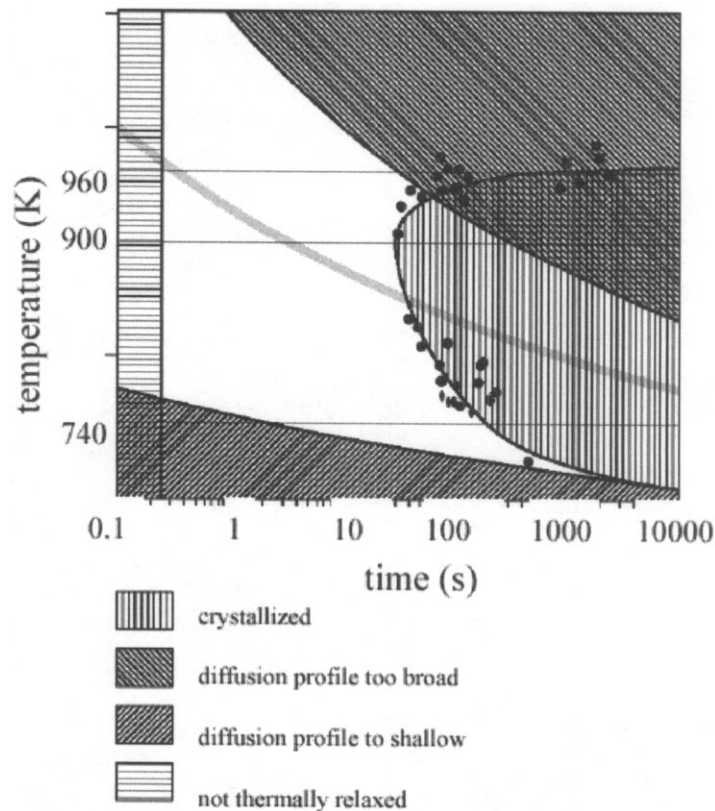


Fig.4 Processing map illustrating the window of opportunity for carrying out Atomic diffusion experiments on a Zr-Nb-Ni-Cu-Al glass forming liquid in both the equilibrium and undercooled regime (down to the glass transition at ~ 675 K).

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NANOLAYERED FEATURES OF COLLAGEN-LIKE PEPTIDES

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Abstract

We have been investigating collagen-like model oligopeptides as molecular bases for complex ordered biomimetic materials. The collagen-like molecules incorporate aspects of native collagen sequence and secondary structure. Designed modifications to native primary and secondary structure have been incorporated to control the nanostructure and microstructure of the collagen-like materials produced. We find that the collagen-like molecules form a number of “lyotropic rod” liquid crystalline phases, which because of their strong temperature dependence in the liquid state can also be viewed as “solvent intercalated thermotropic” liquid crystals. The liquid crystalline phases formed by the molecules can be “captured” in the solid state by drying off solvent, resulting in solid nanopatterned (chemically and physically) thermally stable (to >100°C) materials. Designed sequences which stabilize smectic phases have allowed a variety of nanoscale multilayered biopolymeric materials to be developed. Preliminary investigations suggest that chemical patterns running perpendicular to the smectic layer plane can be functionalized and used to localize a variety of organic, inorganic, and organometallic moieties in very simple multilayered nanocomposites. The phase behavior of collagen-like oligopeptide materials is described, emphasizing the correlation between mesophase, molecular orientation, and chemical patterning at the microscale and nanoscale. In many cases, the textures observed for smectic and hexatic phase collagens are remarkably similar to the complex (and not fully understood) “helicoids” observed in biological collagen-based tissues. Comparisons between biological morphologies and collagen model liquid crystalline (and solidified materials) textures may help us understand the molecular features which impart order and function to the extracellular matrix and to collagen-based mineralized tissues. Initial studies have utilized synthetic collagen-like peptides while future work will also focus on similar sequences generated via genetic engineering methods.

Introduction

Helicoids in Biology

Cholesteric phases can be obtained from highly simplified model collagen molecules and solidified to produce model “helicoid” materials with their cholesteric orientation intact.¹ An unexpected, but not surprising, feature of many of these model collagen molecules is the large number of smectic phases observed as the drying temperature is lowered. The collagen model molecules are very well behaved thermotropic (temperature dependent) liquid crystal mesogens in concentrated solution, generating a series of cholesteric, smectic A*, smectic C* and hexatic and crystalline phases as their drying temperature is lowered. The dried materials resulting from these phases have optical textures and surface morphologies which resemble a number of collagen-based tissues and other biological structures, many of which are difficult to rationalize in terms of simple cholesteric orientation. In a smectic liquid crystal, the molecules (or other rigid rods) are aligned and can have a helicoidal pattern of orientations. Smectic phases also

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feature molecules (or other rigid rods) arranged in regular layers, rather analogous to membranes. Thus smectics have some positional order, whereas the positions of molecules (rigid rods) in a cholesteric are uncorrelated (see for example, Fraden)²⁻⁶. A smectic helicoid will form a material with a sinusoidal variation in orientation and a pattern of chemically distinct regions, defined by the ordered positions of groups or substructures on the rigid rod molecule.

A number of workers have investigated helicoidal arrangements of molecules, fibers, crystals, and fibrils in tissues and in structural biomaterials.⁷⁻¹⁸ The arrangement of basic units (molecular or supermolecular) in these biological helicoids is typically compared to a cholesteric liquid crystalline phase with two caveats: (1) additional features and order are apparent in the biological helicoids that are not present in cholesteric liquid crystals, and (2) the helicoids are solid state materials and not liquid crystals.

Many studies on helicoids have focused on collagen molecules and collagenous tissues. Early work in this area led to the identification of a number of collagenous tissues and collagen-based biological structures which possess geometrical features that can be considered helicoidal. In some cases microscope images suggesting complex arrangements of objects could be more simply and completely accounted for as projection through a helicoid or as helicoidal fracture surface. Reconstruction of these images using helicoidal models has provided new insights into the structure and geometry of tissues and in some cases offered an empirically demonstrated revised model for the ultrastructures of common tissues such as bone.

More recently, several studies have associated biological helicoids with liquid crystallinity – in the liquid state – of precursor molecules. Girauard Guille and coworkers have demonstrated liquid crystalline cholesteric phases in vitro for collagen fibers and triple helical molecules through a systematic series of studies^{12,14-16,19} which have done much to advance the idea of liquid crystalline precursor phases for helicoids. In “Biology of Fibrous Composites”, Neville has recently compiled an “atlas” of helicoids.²⁰ He advances the possibility of blue phases (crisscrossed cholesteric cylinders) as additional helicoidal precursors.

The possibility of helicoids from more highly oriented precursor phases, such as smectic and hexatic phases, has been largely ignored. Smectic phases are more varied and complex than simple nematics and cholesterics and many of the general compilations and treatises on liquid crystals do not cover the smectics fully. Furthermore much of the published characterization of smectic phases relies on a variety of methods to characterize order and orientation. With a few notable exceptions, the literature on helicoids has been dominated by polarizing optical microscopy and electron microscopy and tomography studies. Thus comparisons between the biology oriented studies and the physical characterization studies available for smectics can be difficult. There is thus a need not only to establish smectic phases as likely helicoid precursors, but to also provide data that bridge the two fields and allow comparisons between helicoids (biology) and smectic phases (physics) to be made.

In the present work, a set of polarizing optical micrographs showing typical optical textures and defect patterns for biological smectics, in this case model collagens, has been combined with more quantitative and direct corroborating data on the same samples. These results provide evidence that biological rigid rod molecules can form chiral smectic liquid crystalline phases. A role for smectic phases in collagenous tissue formation is suggested. In addition, a set of optical textures from identified biological smectic

phases is provided by these studies. The model collagens studied thus provide an ideal basis to determine what a smectic-based helicoid would “look like” in terms of typical defect textures, surface morphology, fracture surfaces, anchoring and orientation effects, and overall optical texture (crossed polarizers).

Collagen-like Peptides – Sequence Designs

Repetitive peptides and polypeptides have been studied previously, by a number of workers, to elucidate very general sequence dependencies of collagen structure. Typically a simplified hexapeptide or tripeptide motif is used to build up a longer collagen-like molecule through repetition. Examples include “Gly-Pro-Pro” used to make (Gly-Pro-Pro)₁₂, and “Gly-Ala-Pro-Gly-Pro-Ala” as the basis for a polymer, poly(Gly-Ala-Pro-Gly-Pro-Ala). Early work by Scatturin, Traub, and others established minimum conditions for triple helix formation and stability. These include a high proportion of imino acid residues and the presence of glycine at every third position in the sequence. The second point has recently been confirmed in single crystal studies on short collagen-like peptides. Early workers also established sequence pattern – triple helical conformation – thermal stability trends. Recent work by a number of groups, most notable those led by Goodman and by Fields, have established the thermal and concentration dependent stability for triple helices in solution for a large number of sequence patterns and lengths. A large quantity of data now exists, and the helix melting point for simple repetitive collagens can in many cases be predicted from these data. Our models utilized the wealth of available sequence-stability data in sequence design. The hexapeptide motifs (Gly-Ala-Pro-Gly-Pro-Ala), (Gly-Val-Pro-Gly-Pro-Pro), (Gly-Ala-Pro-Gly-Pro-Pro), (Gly-Ser-Pro-Gly-Pro-Pro), and (Gly-Pro-Ala-Gly-Pro-Pro) were chosen to provide a range of comparable sequences which would allow sequence dependent effects on morphology to be identified.

Experimental

Peptides containing six repeats of each hexapeptide motif were synthesized at the Tufts Protein Core facility at the Sackler School of Medicine. All of the motifs were synthesized with glutamic acid ends as solubilizing blocks. The glutamic acid solubilized oligopeptides which were synthesized thus had sequences:

E ₅ (GAPGPA) ₆ E ₅	Peptide “CPE1”
E ₅ (GAPGPP) ₆ E ₅	Peptide “CPE2”
E ₅ (GVPGPP) ₆ E ₅	Peptide “CPE3”
E ₅ (GSPGPP) ₆ E ₅	Peptide “CPE4”
E ₅ (GPAGPP) ₆ E ₅	Peptide “CPE6”

In addition variants of two of the collagen forming sequence motifs were synthesized with polar asparagine solubilizing ends instead of glutamic acid. The polar interaction between asparagine residues is expected to be attractive, and to encourage triple helix formation. The glutamic acid ends can be repulsive (under conditions where they are charged) or attractive depending on their degree of ionization. The two additional oligopeptides synthesized and studied were:

N ₅ (GAPGPP) ₆ N ₅	Peptide “CPN2”
N ₅ (GPAGPP) ₆ N ₅	Peptide “CPN6”

The synthetic oligopeptides were found to be soluble to concentrations in excess of 200 mg/ml in pure water. The oligopeptides are also ethanol soluble to concentrations up to 100 mg/ml, depending on the individual peptide sequence. Providing temperature, solvent, drying geometry and substrate are controlled, the phase behavior observed is insensitive to concentration changes for concentrations from 100–200 mg/ml. At very low starting concentrations of oligopeptide, different optical textures are observed. The solid dried

films from low concentration solutions are extremely thin and surface effects may dominate the textures formed. Strong surface orienting effects have been observed in some of our previous work on collagens. Very high starting concentrations also produce unusual optical textures. Solution concentrations of 100-200 mg/ml in water and ethanol were used to prepare solid films. Droplets (10 μ l) were cast onto glass slides and either dried uncovered in a dust free location, or covered with a coverslip (but not sealed). Samples were dried at temperatures in the 0-5°C range, focusing on temperatures bracketing 0.7, 1, 2, and 3°C where changes in morphology have been observed to occur.

Dried films were used for the majority of characterization studies. However a few experiments demonstrating the liquid crystalline nature of the films were also prepared. In these cases films were prepared with coverslips as above. Optical textures were observed in the liquid state, and then part of the coverslip was broken off by gentle lifting. The effect on the optical texture was observed. Comparison between the deformed liquid (coverslip lifted) and the areas still intact under the remaining piece of coverslip could be made. Samples were also allowed to dry around the edges. In this situation, when part of the coverslip was fractured/lifted off, intact and stressed contiguous regions in the wet and dry states could be compared.

Characterization - Molecular

A key feature of collagen triple helices is their triple helical conformation, which allows them to behave as rigid rods and to exhibit thermotropic liquid crystallinity in concentrated solution. The secondary structure of the collagens in dried samples was evaluated using wide angle X-ray measurements and FTIR spectroscopy, as described in previous work.

Characterization – Microscopy

Polarizing optical microscopy was used to obtain pictures of textures and to observe the angular dependence of optical extinctions within the sample. Oriented domains can be identified in this manner and a large number of liquid crystalline phases can be “fingerprinted” and identified through comparison with the liquid crystal literature. Because the measurements rely on a qualitative record of birefringence in the sample, little data is obtained regarding the optical properties and absolute (as opposed to relative) orientation of the rods. Field emission scanning electron microscopy (FESEM), a high resolution version of SEM with resolutions on the order of 1 to several nm, was used to examine the surfaces of the samples. The FESEM was used to look for evidence of crystalline spherulites, characteristic helicoidal surface and fracture textures, and to look for evidence of smectic organization in the samples such as terracing. In some cases images of individual smectic layers (in neat stacks) were obtained, allowing an estimate of the smectic layer spacing. Standard electron microscopy was also used to examine fracture and free surfaces of samples.

Characterization – Quantitative

Spatially resolved laser ellipsometry was used to quantitatively map the optical properties of a number of films. Small angle X-ray scattering provided direct evidence of smectic layers. In some cases the layered structures are sufficiently extensive and periodic to produce a large number of X-ray reflections which are orders of the layer spacing. In these instances the orders of the layer spacing show up in WAXS and WAXD measurements.

Results

FTIR spectroscopy indicates a shift in the Amide A vibration to higher wave numbers (higher frequencies and shorter wavelengths) as the preparation temperature for the peptides is lowered. Under conditions where cholesteric and smectic phases are observed, Amide A bands typical of triple helices are observed. The FTIR behavior of the peptides in the triple helical and non-triple helical conformations have been described previously.

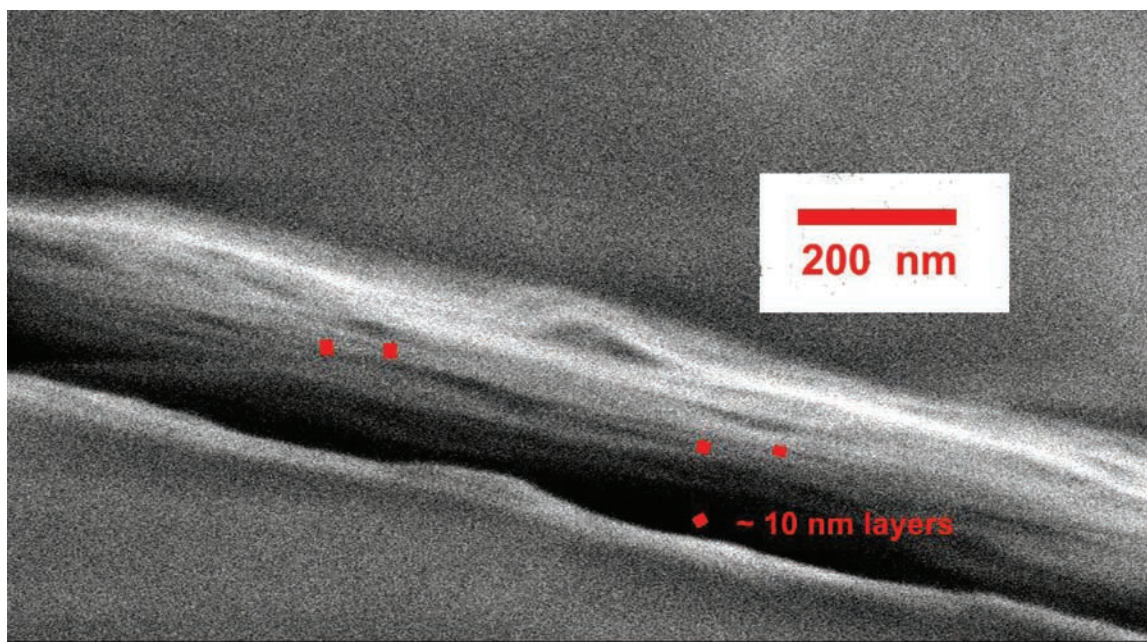


Figure 1. Dried thick film of CPE4 in the smectic A* phase, 2°C. A large number of stacked, roughly 10 nm layers are visible. Two sets of layers are denoted with short black lines in the figure.

Cholesteric phases are observed for collagen-like model peptides dried at 4-5°C, and can be identified in the polarizing microscope. A detailed study of these materials was presented previously. In our prior study we demonstrated that a sinusoidally varying molecular orientation results in a solid surface with sinusoidal variations in surface chemistry. In the model collagens used, a hydrophobic triple helical center block was combined with acidic hydrophilic ends. Twisting of the molecules results in periodic availability of the ends. As reported previously, a number of the films dried in this temperature range display crisscrossed patterns or bands periodically broken by jogs. Because these occur at temperatures intermediate between the cholesteric and smectic A* phases, these textures suggest a TGBA* phase.

At 2-3°C, depending on the peptide sequence, smectic layers are observed. FESEM images of films of CPE4 and CPE6 dried at 2°C allow direct visualization of smectic layers, as shown in Figure 1 for CPE4. The resolution of the FESEM, operated at 1 kV is close to 2 nm. In the Figure, the layers are ~10 nm or 100 Å apart, a value in accord with the length of a 36 residue triple helix with a rise per residue of approximately 2.8 Å – on the order of 110 Å. Lower resolution images of flakes of CPE4 and CPE2 (3°C) reveal several length scales of sinusoidal orientation patterns and undulating layer packing. This type of hierarchical smectic A* texture has been reported previously, by other workers, in studies of smectically ordered poly(benzyl L-glutamate), an α -helix used to obtain a smectic A* phase. The formation of hierarchical length scales of sinusoidal texture can be rationalized in terms of the orientation and layer packing in a smectic A* phase and is likely a hallmark of smectic A*-based helicoids.

Optical microscopy of these phases is difficult because the smectic layers will often align with the glass slide, resulting in a “pseudoisotropic” smectic phase. Here the long axes of the collagen triple helical “rods” are, on average, perpendicular to the glass slide. Unusual concentric circular optical and cracking patterns are typical, and occur along defects which develop in the liquid phase as the films dry. At 1°C a filamentous TGB* optical texture is observed (Figure 2), resulting in a solid with a distinctive “filamentous” surface texture for several of the peptides. SEM studies indicate a high surface area “filamentous” topography associated with the observed optical texture, however the light and dark stripes banding the individual filaments are an optical/orientation phenomenon. The filamentous texture occurs in a narrow temperature range and smectic C* characteristic optical textures and defects are observed at lower temperatures. Thus the filamentous phase may be a TGBC*, but further characterization is needed.

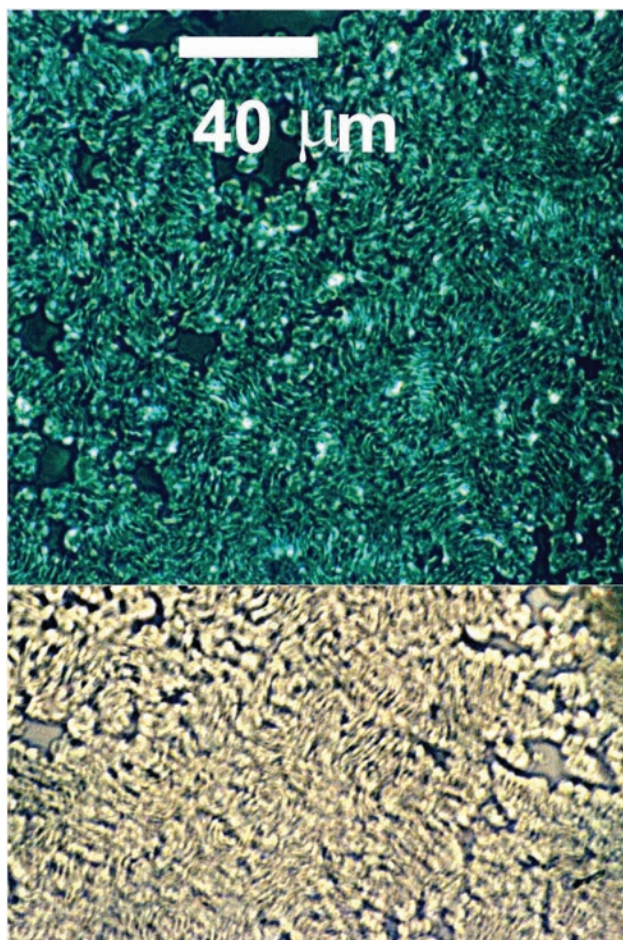


Figure 2. Top - polarizing optical micrograph of filamentous collagen phase from CPE6, 1°C. Bottom - Brightfield optical micrograph (without crossed polars) of the lower right hand region of the polarized micrograph.

As the drying temperature is lowered further, GPAGPP-based peptides (CPE6, CPN6) enter a smectic C* phase with very characteristic optical textures (Fig 3 – CPN6) at temperatures between 0.7°C and 1°C. Hexatic inclusions occur at the lower end of this temperature range. X-ray measurements, including synchrotron SAXS are being conducted. Preliminary data validates the layer spacing of approximately 110 Angstroms, and rods tilted 10° to the layer normal. Quantitative spatially resolved ellipsometric studies indicate very small variations in “rod” orientation as extinction lines and light and dark bands are

crossed, and rod tilts (preliminary) in good agreement with the X-ray data. This result rules out cholesteric order for the optical patterns, and supports a highly aligned smectic phase. In contrast the rods in a cholesteric change their orientation by 180° between light and dark bands) in a sinusoid, and have non-sinusoidal variations in intensity at different orientations as described in detail in the existing literature on cholesteric helicoids.

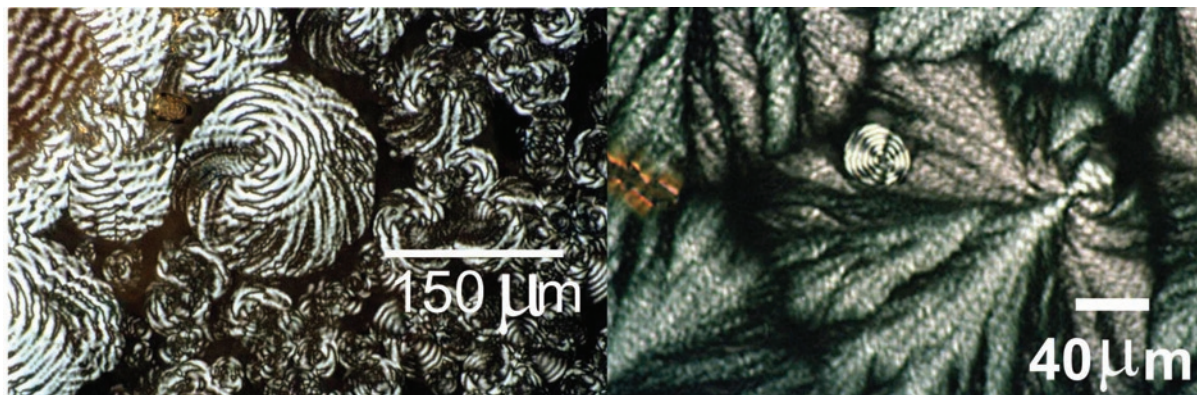


Figure 3. Left (a) smectic C* zig zag texture observed for CPN6 at 1°C. Right (b) Hexatic inclusion in CPE6 at 0.7°C.

Discussion

A number of chiral smectic phases have been observed in simple model collagen oligopeptides dried from high concentration (>100 mg/ml) solutions at subambient ($0\text{--}3^\circ\text{C}$) temperatures. An orderly progression from smectic A* to smectic C* and hexatic phases is observed for several of these peptides as the drying temperature is lowered. The morphology and orientation of the phases as well as the temperatures at which they occur are sequence dependent. All of the liquid crystalline phases can be dried with their optical textures intact, allowing techniques such as high resolution scanning electron microscopy to be used to directly visualize smectic layers. The dried “liquid crystal” materials formed from smectic and hexatic phases strongly resemble a number of biological helicoids which possess orderly features not well addressed by simple cholesteric models for their orientation and order. Thus collagen smectic formation is a highly biomimetic process, resulting in materials with many of the features observed in their biological analogues. Collagen fibers consist of staggered layers and are piezoelectric, suggesting a ferroelectric smectic liquid precursor phase. In both cases the collagen molecules are sufficiently well aligned to form layered chemically and physically distinct regions which exist in a regular pattern throughout the collagen material. Cholesterics, in contrast, have more disordered orientations and are characterized by slow change in average orientation of the chiral rods and do not have localized chain ends.

The observations reported here, combining optical images with ongoing corroborating molecular level details, suggest that collagen peptides are capable of well-defined supramolecular assembly when placed within appropriate environmental conditions at suitable concentrations. Furthermore, these observations at low temperatures can be easily translated to higher temperature more biologically relevant systems simply by modulating the hydroxylation content of the prolines in the sequences; a feature well-documented in the literature related to collagen triple helix formation. Changes in the overall collagen triple helix sequence length, or the polarity of the solvent used to prepare the materials also impact the liquid crystalline behavior of the model collagens and are actively being investigated as avenues to control structure.

With the design and implementation of these new collagen triblock systems, new opportunities to study relationships between collagen sequence and hierarchical assembly can be realized. This insight has major significance to fundamental concepts in liquid crystal phase formation as well as to the impact of microgravity on these phases. Furthermore, this level of understanding offers options for future model systems with which to study the impact of microgravity on materials assembly as well as tissue structure and function in vitro and in vivo. It is also important to point out that the current work has been focused on synthetically derived collagen model peptides which are necessarily limited in molecular weight and availability. Ongoing efforts are aimed at overcoming these limitations through genetic engineering in order to manipulate polymer chain length, sequences and to deal with larger levels of production.

Acknowledgements

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PHASE-FIELD SIMULATIONS OF THREE-DIMENSIONAL DENDRITIC GROWTH AT LOW UNDERCOOLING

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Introduction

Commercial metallic alloys often freeze dendritically. The microstructure that results from this nonequilibrium process controls the properties of the final solidification product. Moreover, dendritic growth has been of fundamental interest to physicists in the general context of pattern formation in non-equilibrium dissipative systems.

Even though dendrites have been studied for decades, our present understanding of the growth of these structures remains in many cases uncertain and/or qualitative. Sharp-interface theories have been developed that make explicit predictions for (i) the tip steady-state operating state (tip velocity V and tip radius ρ) [1], (ii) the three-dimensional tip morphology [2,3], and (iii) the formation of secondary branches (sidebranching) [4,5]. These theories, however, generally assume that the transport in the melt is purely diffusive, whereas dendrite growth in terrestrial experiments is strongly influenced by convection. For this reason, the predictive capability of these theories has remained largely untested.

Recent advances in the phase-field method have created a unique opportunity to accurately test these theories. This method has the well-known advantage that it avoids front-tracking by the use of a scalar field that distinguishes between solid and liquid. Improved phase-field formulations [6] and efficient algorithms [7] are now making it possible to simulate dendrite growth in three dimensions, in both transient and steady-state growth regimes. In this report, we summarize the recent progress made in using state-of-the-art phase-field simulations to test accurately the predictions of sidebranching theories based on noise amplification, as well as to investigate whether thermal noise of microscopic origin suffices to produce the experimentally observed sidebranching activity.

Phase Field Simulations

We study the crystallization of a pure undercooled melt that is governed by the standard set of equations that consists of the heat diffusion equation, the condition of heat conservation at the interface, and the Gibbs-Thomson condition assuming local equilibrium at the interface. Aside from material constants that can be scaled out, morphological evolution is controlled by three basic dimensionless parameters: Δ , ε , and F_{exp} , defined by:

$$\Delta = \frac{T_M - T_\infty}{L/c}$$
$$\gamma = \gamma_0 (1 + \varepsilon \cos 4\theta)$$
$$F_{\text{exp}} = \frac{k_B T_M^2 c}{L^2 d_0^3}$$

Keywords: dendrites, sidebranching, noise, anisotropy, phase-field

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Δ is the melt undercooling scaled by the ratio L/c of the latent heat of melting and the bulk specific heat, ε is the magnitude of the anisotropy of the excess free-energy γ of the solid-liquid interface, i.e. of the four-fold variation with orientation θ in a (100) plane, and F_{exp} is a dimensionless measure of the strength of thermal fluctuations of microscopic origin, where k_B is the Boltzmann constant and $d_0 = \gamma_0 T_M c / L^2$ is the capillary length.

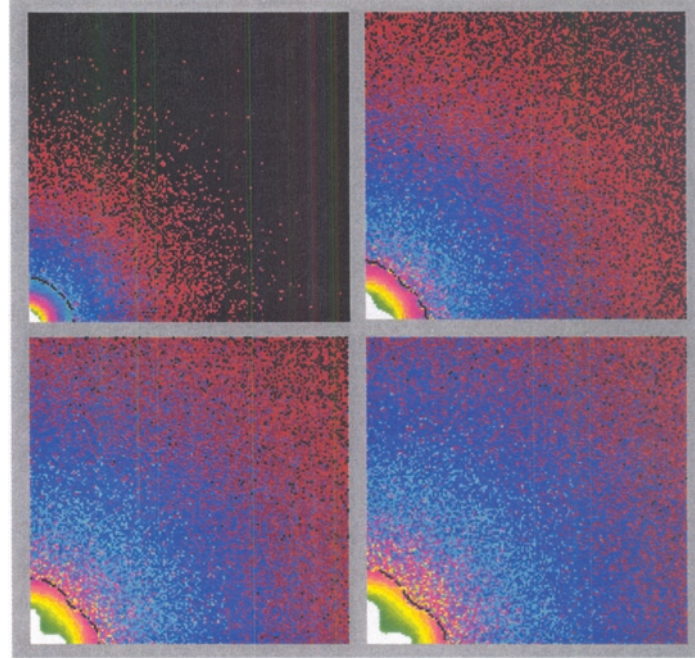


Fig. 1 Snapshots of phase-field simulations of the growth of a two-dimensional crystal seed using a hybrid finite-difference diffusion Monte Carlo algorithm for $\Delta=0.02$ and $\varepsilon=0.025$. Time increases from left to right and top to bottom. The solid is shown in white. The colors represent the thermal field computed using a standard finite difference discretization of the diffusion equation in the solid and a thin liquid layer surrounding the interface, and with a large ensemble of random walkers in the rest of the liquid that comprises the outer diffusion boundary layer. Walkers take progressively larger and less frequent steps with increasing distance away from the interface, which makes the computation time scale roughly like the volume of the growth structure instead of the much larger volume of liquid.

Our simulations combine several improvements of the phase-field method that make quantitative modeling at low undercooling feasible. Firstly, we use the thin-interface limit of the phase-field model developed by Karma and Rappel [6], which allows us to choose the interface thickness in the phase-field model one to two orders of magnitude larger than the microscopic capillary length d_0 . Secondly, we use a hybrid finite-difference diffusion Monte Carlo algorithm [7] (illustrated in Fig. 1) that solves efficiently the diffusion equation within the large scale thermal boundary layer that surrounds the growing crystal. Thirdly, we incorporate thermal fluctuations in the model by using a Langevin formalism [8]. This formalism consists of adding stochastic variables to the phase-field equations. These variables are uncorrelated in both space and time and obey Gaussian distributions whose variances are fixed by the fluctuation dissipation theorem. The latter is simply the thermodynamic self-consistency requirement that the stochastic phase-field equations should reproduce the known spectrum of thermal fluctuations in equilibrium ($\Delta=0$).

In order to reduce the computation time further, we exploit the cubic symmetry of the crystal and only simulate the growth of 1/8 of a single dendrite arm, i.e. with the polar angle in the plane perpendicular to the growth

axis ranging from 0 to 45 degrees. In addition, to properly study the development of sidebranches behind the tip of this arm, we need to reach a steady-state growth regime, which requires long simulation times. To achieve this, we periodically translate the arm inside the computational box by cutting the interface at a finite distance from the tip. We have verified that this treadmill procedure does not significantly influence our results if this distance is chosen large enough.



Fig. 2 Snapshots of the solid-liquid interface illustrating the development of sidebranches after thermal noise is turned on in the phase-field simulation, with time increasing from left to right and the parameters $\Delta=0.1$, $\varepsilon=0.025$, and $F_{\text{exp}}=0.01$. The small initial amplitude of sidebranching in the left picture is due to the random-walker noise that is negligibly small in comparison to the thermal noise incorporated by adding Gaussian random variables to the phase-field equations.

Results

We have carried out computations for values of Δ ranging from 0.1 to 0.2, corresponding to Peclet numbers in the range of 0.01 to 0.1 (where the Peclet number is defined by $Pe=\rho V/(2D)$, and D is the thermal diffusivity), ε values ranging from 0.0125 to 0.025, and F_{exp} ranging from 10^{-3} to 10^{-1} . The sidebranching activity is studied by recording time traces of the $x(z,t)$ coordinate of the interface in the (100) plane for different distances z from the tip along the growth axis as illustrated in Fig. 3. We compute from these traces the mean sidebranch amplitude $A(z)$ and spacing $\lambda(z)$ defined by

$$A(z) = \sqrt{\langle x(z,t)^2 \rangle - \langle x(z,t) \rangle^2}$$

$$\lambda(z) = 2Vt_0/N(z)$$

where $\langle \rangle$ denotes a time average over a time interval t_0 , and $N(z)$ is the number of extrema of $x(z,t)$ (i.e. zero crossings of $dx(z,t)/dt$) during the same time interval. Given the computing time available for each run, we are able to study time intervals where N is about 20, which is sufficient to obtain statistically meaningful averages.

We compare our simulation results to the predictions of noise amplification theory [4,5] for the sidebranch amplitude and spacing given (for an arbitrary shape) by [9]

$$\tilde{A}(\tilde{z}) \approx A_0 \exp \left[\frac{2}{3} \left(\frac{\tilde{x}^3}{3 \sigma(\varepsilon) \tilde{z}} \right)^{1/2} \right]$$

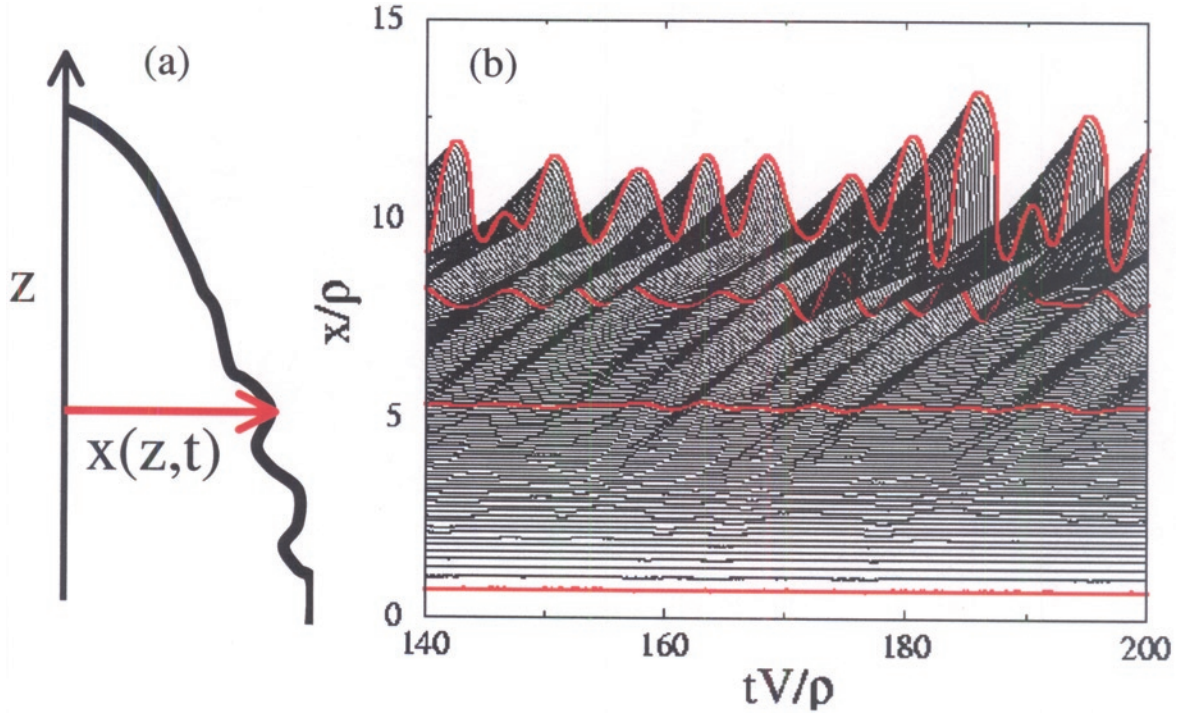


Fig. 3 (a) Schematic representation of a section of the dendrite arm in a (100) plane used to measure the half width $x(z,t)$. (b) superimposed time plots of this width for different distances z behind the tip for $\Delta=0.1$, $\varepsilon=0.025$, and $F_{\text{exp}}=0.1$; four of these plots are highlighted in red.

$$\tilde{\lambda}(\tilde{z}) \approx \left[\frac{12\pi^2 \sigma(\varepsilon) \tilde{z}}{\tilde{x}} \right]^{1/2}$$

where all lengths with tilde are scaled by the tip radius ρ ,

$$A_0 \approx \left[\frac{2k_B T^2 cD}{L^2 \rho^4 V} \right]^{1/2}$$

and $\sigma(\varepsilon)=2d_0 D/(\rho^2 V)$ is the usual selection constant that, for the low undercoolings simulated here, depends only on the anisotropy strength ε . For the comparisons with our simulations, we use the average tip shape $\langle x(z,t) \rangle$ extracted from the simulation data.

In Fig. 4, we show results for the sidebranch amplitude for various undercoolings and anisotropies. These results show that the predictions of noise amplification theory work reasonably well in that the predicted amplitude is of the right order of magnitude without any fit parameter. Moreover, the several orders of magnitude exponential increase of the sidebranch amplitude with z is reasonably well predicted, even quantitatively. The larger deviations far down the shaft (large z/ρ) can be attributed to the onset of nonlinear effects (i.e. the early stage of sidebranch coarsening) which are not included in the theory.

The agreement becomes even more convincing when one considers the dependence of the amplitudes on undercooling Δ and anisotropy strength ε separately. The theoretical prediction is the product of a global prefactor that depends on the tip parameters of the dendrite and the dimensionless noise strength F_{exp} , and a z -dependent part that only depends on the scaled shape of the dendrite. As has been predicted theoretically [4] and recently confirmed by phase-field simulations [10], the scaled shape is independent of anisotropy

and undercooling for the parameter range of our simulations. We have plotted in Fig. 4(b) the extracted mean shapes for two different anisotropies, and they indeed superpose very nicely. Consequently, the z dependence of the sidebranch amplitude depends only on the selection constant σ , which is a constant for fixed ε . Therefore, amplitudes for different undercoolings should differ only by a global prefactor that is independent of z ; this becomes a constant shift on a log plot. As can be seen in Fig. 4(a), the curves

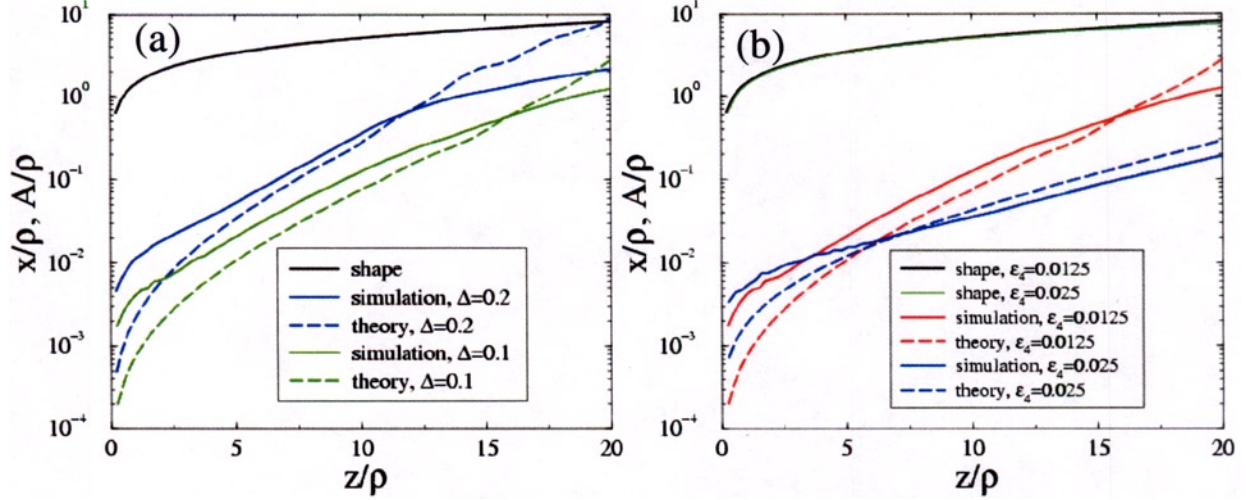


Fig. 4 Plots of steady-state shape x/ρ and sidebranching amplitude A/ρ versus distance z/ρ from the tip for (a) different undercoolings and fixed $\varepsilon=0.025$ and $F_{\text{exp}}=0.01$, and (b) different anisotropies and fixed $\Delta=0.1$ with $F_{\text{exp}}=0.1$ for $\varepsilon=0.025$ and $F_{\text{exp}}=0.01$ for $\varepsilon=0.0125$.

$A(z)$ for two different undercoolings at constant ε are indeed reasonably parallel. In contrast, for equal undercooling but different anisotropies, the amplification rates are clearly different, as shown in Fig. 4(b). The different slopes of the curves in the log plot are well predicted by the theory.

In summary, we find a good overall agreement between our simulated sidebranch amplitudes and the predictions of noise amplification theory. Since, in addition, this theory was successfully compared to experimental data previously [11], we can conclude that thermal fluctuations of microscopic origin suffice to produce the level of sidebranching activity observed experimentally. Of course, this does not rule out the possibility that other sources of noise can be simultaneously present in experiments. Furthermore, our results show that the distance from the tip at which sidebranches become visible decreases with decreasing anisotropy and increasing undercooling. Both of these trends are qualitatively consistent with experimental observations to date. In particular, sidebranches have been observed to form closer to the tip with increasing undercooling in succinonitrile (SCN) [12]. In addition, sidebranches form much further behind the tip in pivalic acid (PVA) than SCN [13], consistent with the fact that PVA is much more anisotropic than SCN.

In Fig. 5, we show the sidebranch spacing vs distance from the tip for various undercoolings, anisotropies, and noise strengths. While the overall agreement with theory is not very good, some qualitative features of the theory are nevertheless reproduced. Namely, as can be seen from Fig. 5(a), the spacing is, up to statistical errors, independent of the undercooling and the noise strength, which indeed do not appear in the theoretical prediction. Furthermore, as shown in Fig. 5(b), the final spacing decreases with anisotropy, in qualitative agreement with the WKB prediction. However, the z -dependence of the spacing is not reproduced: whereas theory predicts a slowly and monotonously increasing spacing, the simulated

spacings increase sharply close to the tip, pass through a maximum that is more pronounced at lower anisotropy, and saturate to an almost constant value as early as 5 times the tip radius behind the tip. Note that, typically, $A/\rho \sim 0.01$ at that distance, such that branches are still invisible for typical experimental resolutions. Therefore, after sidebranches become visible in experiments their spacing should remain essentially constant, as was indeed found recently [13].

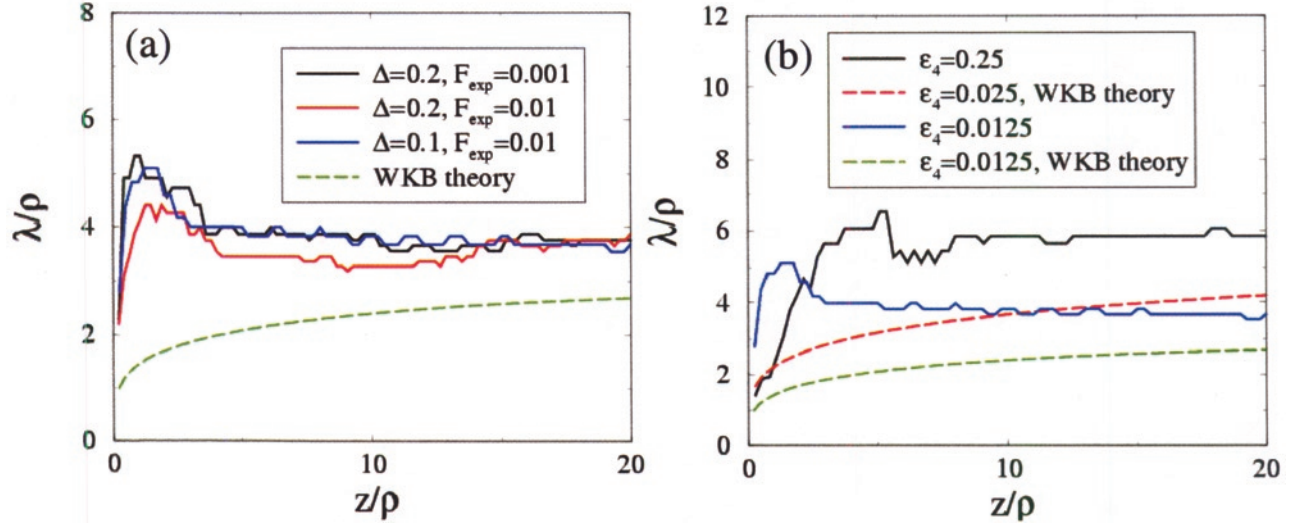


Fig. 5 Plots of sidebranch spacing λ/ρ versus distance z/ρ behind the tip for (a) different undercoolings and noise strengths at fixed $\epsilon=0.0125$, and (b) for different anisotropies and fixed $\Delta=0.1$, with $F_{\text{exp}}=0.1$ for $\epsilon=0.025$ and $F_{\text{exp}}=0.01$ for $\epsilon=0.0125$.

In summary, while the theory qualitatively explains some of the observed trends, it can not be used to make quantitative predictions for the sidebranch spacing. At present, our data analysis is too preliminary to pinpoint more precisely the reasons for the discrepancy between theory and simulations, but more work is in progress.

Conclusions

We have carried out quantitative three-dimensional simulations of dendritic growth at low undercoolings to study in detail the early stage of formation of sidebranches. We find that, remarkably, thermal fluctuations of microscopic origin suffice to produce the level of sidebranching activity observed experimentally, which is the first direct confirmation of this hypothesis. Our results show that both the distance from the tip at which sidebranches become visible and their mean spacing decrease with decreasing anisotropy. Both of these trends are qualitatively consistent with what is experimentally observed and predicted by noise-amplification theory. Furthermore, the several orders of magnitude exponential increase of the sidebranch amplitude with z is reasonably well predicted quantitatively by this theory. The variation of the mean sidebranch spacing with z , however, is not. In the simulations, the spacing increases steeply over a distance of a few ρ and then reaches a plateau after passing through a maximum that is more pronounced for lower anisotropy. In contrast, theory predicts a smooth monotonous increase of the spacing with increasing distance behind the tip. Further work to pinpoint more precisely the reasons for this discrepancy between simulations and theory is currently in progress.

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STUDIES OF NUCLEATION AND GROWTH, SPECIFIC HEAT AND VISCOSITY OF UNDERCOOLED MELTS OF QUASICRYSTAL AND POLYTETRAHEDRAL-PHASE FORMING ALLOYS

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1. Introduction

Fahrenheit first recognized that many liquids can be maintained out of equilibrium (i.e. below the melting temperature) for long periods without crystallizing[1]. The amount of undercooling attainable before solidification is often quite large, up to one third of the melting temperature, as was observed for liquid mercury[2]. Such a dramatic undercooling for a liquid metal is surprising, given the similarity in the densities of metallic liquids and solids, and the similar average interatomic distances and coordination numbers. It is now recognized that all liquids can be deeply undercooled, typically to approximately 20% of their liquidus temperatures[3]. This resistance to crystallization indicates that a substantial barrier separates the initial and final states.

Frank first argued that this transformation barrier arises from different local atomic configurations in the liquid and the crystal[4]. The relatively weak non-covalent bonding in many metals leads to their tendency to crystallize into relatively close-packed structures, which can be usefully modeled by a packing of hard spheres. Face-centered-cubic (fcc) and close-packed hexagonal (cph) are the most densely packed periodic structures. However, an icosahedral packing, is even denser. For a pair-wise central potential, such as the Lennard-Jones potential, the fully relaxed energy of icosahedral packing is, therefore, lower than that of fcc or cph. While icosahedral packing is incompatible with translation periodicity, it might be a natural choice for liquid and amorphous phases. Crystallization would then require that the local icosahedral order be transformed to an allowed crystallographic one, costing energy. This may provide a natural barrier for nucleation of a crystalline phase from the liquid.

The stability of icosahedral clusters is evident in the “magic numbers” for the total atoms in free atomic clusters[5,6]. Further, the results of molecular dynamics simulations and some physical property measurements are consistent with this presumed icosahedral order in liquids. However, it has not been observed directly. Quasicrystals, a new class of condensed matter discovered by Shechtman and co-workers in 1984 [7], have extended icosahedral order. A low interfacial energy for the nucleation of quasicrystals from liquids and glasses[8] is consistent with the existence of similar order in the liquid.

Measurements of the maximum undercooling and growth velocity of undercooled liquids that form quasicrystals and related crystal approximant phases can allow a study of the nucleation and growth mechanisms for complex periodic and ordered nonperiodic phases. Further, since quasicrystals generally

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have a composition different from that of the initial liquid phase, undercooling studies allow an investigation of nucleation processes when the composition of the initial and final phases are different. Quantitative measurements of the melt viscosity and specific heat as a function of alloy composition near the ideal stoichiometry of the phases with icosahedral order can be used to investigate the onset of icosahedral order in undercooled liquids. Undercooling and thermo-physical property measurements can, then, lead to a deeper understanding of the structure of the undercooled liquids, and better inform us of processes that are central in all materials development and production.

Ti-Zr-Ni alloys are particularly well suited for such experiments. Over the past decade this research group has identified many interesting phases in this alloy system. Three that are most relevant for the research under this grant are, a) β -Ti/Zr (bcc) solid solution, b) C14 Laves phase, and c) a stable icosahedral (i-phase) phase. The complexity of the local structure of these phases increases in the order listed above, providing a unique opportunity to study nucleation as a function of increasing polytetrahedral order in the same alloy system. Containerless processing with the electrostatic levitation (ESL) facility at the Marshall Space Flight Center (MSFC), Huntsville, AL, has not only allowed us to study the undercooling behavior of these alloys as a function of composition, but also to make thermo-physical property measurements in the liquid and undercooled state. In addition, the beamline ESL (BESL) facility, recently developed to measure in-situ structural properties using synchrotron radiation at the Advanced Photon Source (APS, MU-CAT) at Argonne National laboratory, has allowed us to make the first studies of the developing icosahedral order in the liquid as a function of undercooling. These ground-based studies have demonstrated the feasibility and need to conduct benchmark nucleation experiments on the International Space Station (ISS). Those results are discussed briefly here.

2. Phase Diagram Determination of Ti-Zr-Ni Alloys

A quantitative analysis of undercooling data requires that the phase diagram be known near the alloy compositions of interest. To investigate this, we have made an exhaustive study of the phase microstructures in as-cast and annealed samples. As-cast ingots (0.5 g) of Ti-Zr-Ni were prepared over a wide composition range ($\text{Ti}_{(25-65)}\text{Zr}_{(20-54)}\text{Ni}_{(2-40)}$) from high-purity elements Ti (99.995%), Zr (99.9%) and Ni (99.995). The as-cast alloys were annealed at various temperatures ($500\text{ }^{\circ}\text{C} < T < 850\text{ }^{\circ}\text{C}$) for various lengths of times. Using x-ray powder diffraction, and scanning and transmission electron microscopy, equipped with energy dispersive x-ray spectroscopy, the equilibrium phases in the as-cast and annealed samples at various temperatures were identified and quantified. Because conventional techniques (DTA, DSC, etc.) are unreliable for highly reactive high melting point alloys, ESL studies were used to determine the solidus and liquidus temperatures of these alloys. A cut of the Ti-Zr-Ni phase diagram for equal Ti and Zr concentrations, constructed from these extensive studies, is shown in Fig. 1 as an illustration. For low Ni ($\leq 5\text{ at.}\%$) concentrations, β -Ti/Zr (bcc, with $a = 3.43\text{ \AA}$ at $700\text{ }^{\circ}\text{C}$ [9]) is the primary solidification phase from the liquid. As the temperature decreases, β (Ti/Zr) undergoes an allotropic transformation (*i.e.* a structural transformation with no change in composition) to α (Ti/Zr) (hcp, $a = 3.12\text{ \AA}$, $c = 4.94\text{ \AA}$) in the temperature range of $550 - 650\text{ }^{\circ}\text{C}$ (depending on the Ti/Zr ratio). With increasing Ni, the liquidus temperature decreases and the alloy becomes a mixture of β (Ti/Zr) and the C14 Laves phase (a polytetrahedral hcp phase with $a = 5.22\text{ \AA}$ and $c = 8.56\text{ \AA}$). Due to the allotropic transformation, the as-cast alloys, however, always contain α (Ti/Zr) instead of β (Ti/Zr).

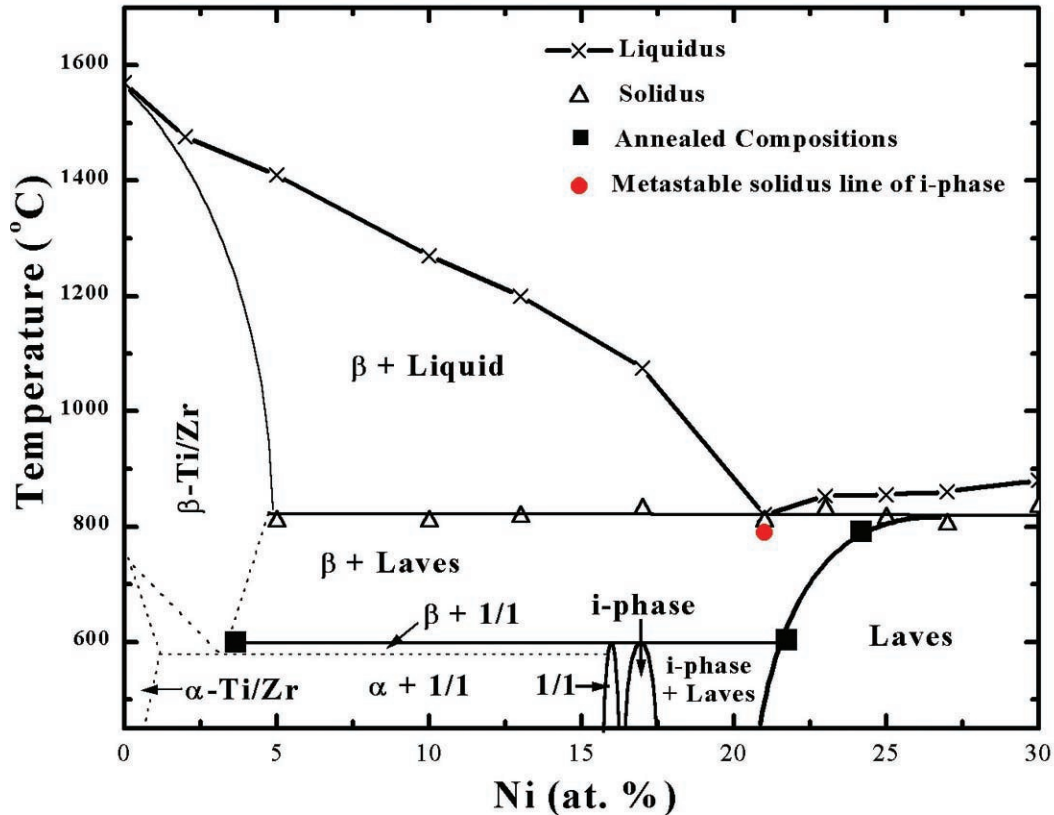


Fig. 1. Vertical section of the Ti-Zr-Ni phase diagram for a Ti/Z ratio equal to one. The symbols are the experimental data and the solid and dashed lines indicate the phase boundaries.

For alloys made with 16-18 at.% Ni, the stable phase for $T < 570$ °C is, surprisingly, not a mixture of $\alpha(\text{Ti/Zr})$ and the C14 Laves phase. Extensive annealing studies over this temperature and composition range show that the lowest temperature phase is either an icosahedral phase with a quasi-lattice constant of 5.21-5.24 Å, or the 1/1 crystal approximant (bcc, $a = 14.32$ Å). One of the important challenges of the ESL undercooling studies was to explore whether the i-phase may become the primary crystallizing phase from the undercooled liquid, if the nucleation of $\beta(\text{Ti/Zr})$ and the C14 Laves phases were avoided.

One interesting feature of the phase diagram is the existence of an eutectic phase around 21 at.% Ni composition. Below the eutectic temperature, $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ should crystallize to a eutectic mixture of the $\beta(\text{Ti/Zr})$ and the C14 phase. As indicated by the filled circle in Fig. 1, recent studies[10] of rapidly solidified droplets at this composition, however, show a recalescence at 700 °C and a solidification plateau at approximately 790 °C, which correspond to the nucleation and growth of the icosahedral phase[10]. This temperature is only slightly below the eutectic temperature. As indicated in the vertical section, extensive investigations have shown that the i-phase is stable only at temperatures below 600°C; no alloy concentration has been found where the i-phase is stable at higher temperatures. As will be discussed soon, this $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ i-phase is actually a metastable solidification product. Nevertheless, it is the primary solidification phase at the cooling rates found in ESL, allowing studies to be made of the nucleation kinetics for the Ti-Zr-Ni i-phase.

Above 25 at. % Ni, the primary crystallizing phase is the C14 Laves phase. The local atomic structure of this polytetrahedral periodic phase is presumed to be similar to that of the i-phase[11]. This provides

another opportunity to study the nucleation of a polytetrahedral phase, in addition to the i-phase, using the MSL-EML on the ISS.

3. Electrostatic Levitation (ESL) Studies

3.1 Undercooling Behavior

Based on the phase diagrams presented in §2 a large number of Ti-Zr-Ni alloys were selected for processing in the electrostatic levitator (ESL) at MSFC. *The primary objective of these ESL studies was to identify the crystallizing phases that nucleate directly from the undercooled liquid, study their undercooling behavior, identify the compositions of most interest for studies using the MSL-EML facility planned for the ISS, and to understand the fundamental process of nucleation of polytetrahedral phase forming alloys.*

Fig. 2 shows the measured sample temperature as a function of time during free radiative cooling in the ESL for some representative Ti-Zr-Ni alloys. These are shown as a function of increasing Ni ($0 < \text{Ni} < 17$ at.%), but for equal Ti/Zr concentrations. A single recalescence event marks the nucleation and growth of $\beta(\text{Ti/Zr})$ for the alloy containing 2 at.% Ni (Fig. 2(a)). The small recalescence at approximately 550 °C is due to the $\beta(\text{Ti/Zr})$ to $\alpha(\text{Ti/Zr})$ transformation. In contrast, the $\text{Ti}_{47.5}\text{Zr}_{47.5}\text{Ni}_5$ alloy shows an additional small plateau near 750 °C (see inset of Fig. 2(b)), signaling the formation of the C14 Laves phase from the remainder of the liquid. The volume fraction of this phase is very small, however, and is not evident in the x-ray diffraction patterns, but it is found in SEM studies of the solidification microstructure. The lower temperature recalescence is much more prominent in the 13 at.% and 17 at.% Ni samples, with a corresponding decrease in the high temperature event. This indicates a decrease in the crystalline volume fraction of the $\beta(\text{Ti/Zr})$ phase and an increase in the volume fraction of the C14 Laves phase as the Ni concentration is increased. These points were further confirmed by powder x-ray diffraction and SEM studies on the ESL processed samples and are consistent with the phase diagram (Fig. 1). The onset temperature of the high temperature recalescence (nucleation of the $\beta(\text{Ti/Zr})$ phase) decreases with increasing Ni, due to a decrease in the liquidus. The reduced undercooling of the $\beta(\text{Ti/Zr})$ phase ($\Delta T_r = (T_m - T_r)/T_m$) increases slightly from 0.16 to 0.20 with increasing Ni; a value typical for simple phase forming alloys.

Interestingly, for alloys containing about 21 at.% Ni (Fig. 3(a)), a two step recalescence is observed. The first plateau temperature is approximately 785 °C and the second plateau temperature, corresponding to the solidus temperature, is approximately 810 °C. The liquidus temperature is about 820 °C. The Ni concentration is critical for the occurrence of the step recalescence; the Ti/Zr concentration is less critical (occurring for $29 \text{ at.\%} \leq \text{Ti} \leq 45 \text{ at.\%}$), however. Based on the phase diagram, the low temperature recalescence *should* correspond to the formation of the C14 Laves phase. The plateau temperature is, however, approximately 25 °C below the expected solidus temperature (810 °C). Were it due to the formation of $\beta(\text{Ti/Zr})$,

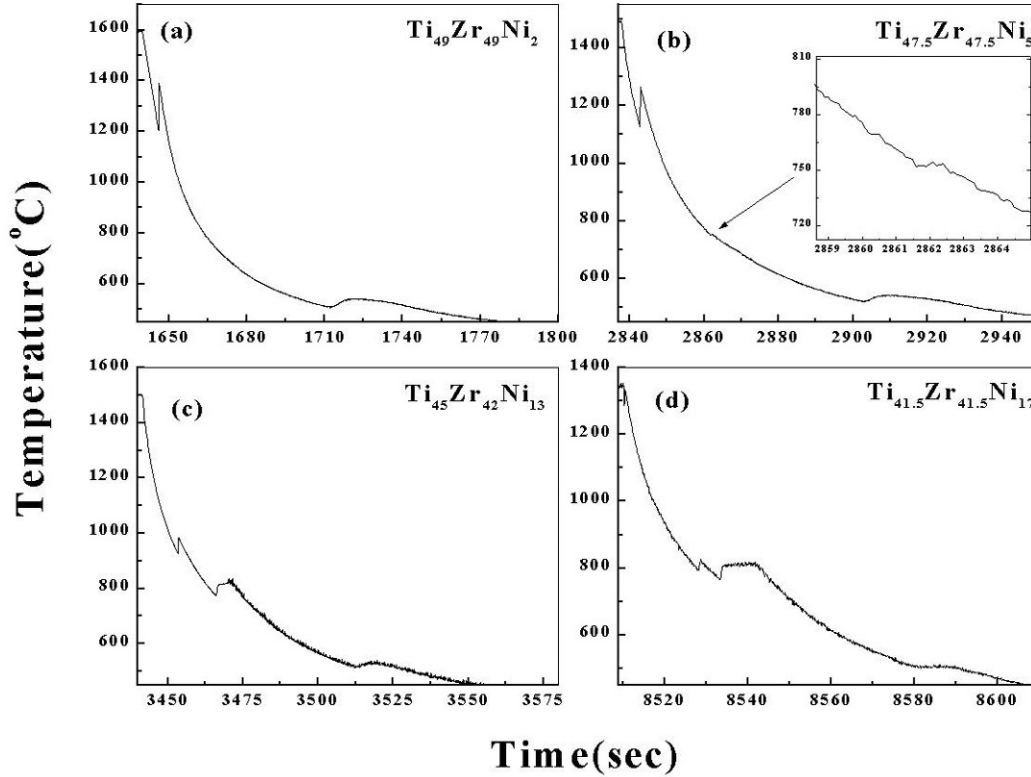


Fig. 2. Temperature-time cooling curves for Ti-Zr-Ni alloys.

the plateau temperature should be even higher. Further, the reduced undercooling for this alloy (≈ 0.12) is much smaller than is typically observed for the $\beta(\text{Ti/Zr})$ phase (0.18 on the average). Although the recalescence events are inconsistent with the nucleation of either the C14 Laves or the $\beta(\text{Ti/Zr})$ phase, the x-ray diffraction pattern or the SEM micrographs of these ESL processed alloys show a phase mixture of C14 Laves and the $\beta(\text{Ti/Zr})$ phase. This apparent contradiction was resolved by in-situ x-ray diffraction studies during recalescence in the beamline ESL (BESL), as will be demonstrated in the next section.

Alloys containing 25 at.% and higher amounts of Ni, show a single recalescence event (Fig. 3(b)-3(d)). X-ray and SEM studies indicate the presence of primarily the C14 phase, and a small volume fraction of the $\alpha(\text{Ti/Zr})$ phase for the alloys containing about 25 at. % Ni. For the $\text{Ti}_{40}\text{Zr}_{30}\text{Ni}_{30}$ alloy, pure C14 phase is observed, confirming primary nucleation of this phase directly from the undercooled liquid. The reduced undercooling for the Laves phase was found to be about 0.14, smaller than for the $\beta(\text{Ti/Zr})$ phase (0.18 on the average).

3.2 The primary nucleating phase in $\text{Ti}_{79-x}\text{Zr}_x\text{Ni}_{21}$ alloys

The fact that the recalescence events for these alloys are inconsistent with the nucleation of either the C14 Laves or the $\beta(\text{Ti/Zr})$ phase, raises the possibility that the nucleating phase is metastable. If the first temperature rise is due to the nucleation and growth of a metastable phase, then the second thermal event could be associated with the subsequent decomposition of the metastable phase into the stable C14 Laves and the $\beta(\text{Ti/Zr})$ phases. The identification of such short-lived metastable phases is not easy, however. In-situ x-ray or neutron diffraction studies coupled with containerless processing and fast detectors, is the only direct method for the unambiguous identification of such metastable phases. The BESL facility has

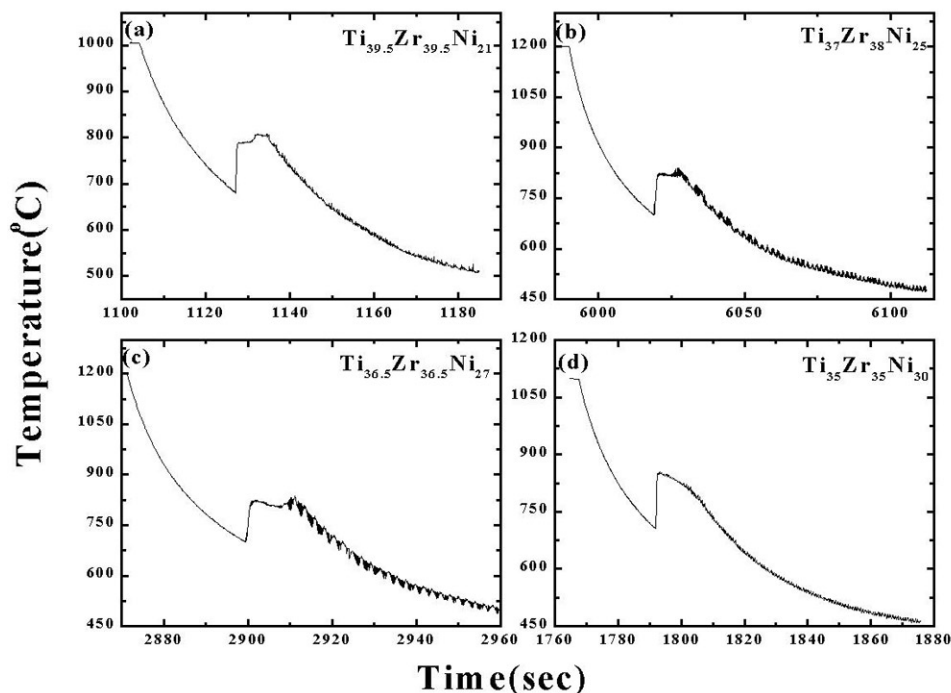


Fig. 3. Temperature-time cooling curves of undercooled Ti-Zr-Ni alloys.

been recently developed jointly by our group at Washington University, the NASA-ESL group led by J. Rogers, and representatives of MU-CAT at the Advanced Photon Source (APS), led by A. I. Goldman. This facility was recently used to study the structure and phase transitions of highly undercooled liquids of high temperature alloys using containerless processing techniques under high vacuum. The high flux synchrotron x-ray source, coupled with an image-plate detector, enabled BESL to acquire a complete set of diffraction data over a q -range from 0 to $8 \text{ \AA}^{-1}$ in less than one second. Fig. 4 shows the first results of in-situ x-ray diffraction studies on an electrostatically levitated liquid droplet. These were obtained from a $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ alloy at $756 \text{ }^\circ\text{C}$ in the undercooled liquid state, during and after recalescence. The image plate was exposed typically for about 1 s to obtain each diffraction pattern.

These data clearly indicate that the liquid transforms to the i -phase during recalescence, subsequently transforming to a phase mixture of the C14 Laves and the $\beta(\text{Ti/Zr})$ phases after recalescence, all within a few seconds. This is direct proof that the i -phase nucleates first from the undercooled liquid. The rise in temperature during recalescence drives its decomposition into the C14 Laves and the $\beta(\text{Ti/Zr})$ phases. The composition range over which the i -phase nucleates directly from the liquid is, however, restricted ($20.5 \text{ at.\%} < \text{Ni} < 21.5 \text{ at.\%}$, $29 \text{ at.\%} < \text{Ti} < 45 \text{ at.\%}$). Our ground-based experiments, therefore, clearly identify three composition ranges in Ti-Zr-Ni alloys where the $\beta(\text{Ti/Zr})$, the Laves phase, and the i -phase are the primary nucleating phases from the undercooled liquid. The most important result is that ***the maximum reduced undercooling decreases from 0.18 ($\beta(\text{Ti/Zr})$) to 0.14 (Laves) to 0.12 (i -phase) with increasing polytetrahedral order of the solid.*** These results strongly support Frank's hypothesis and are in agreement with earlier electromagnetic levitation (EML) undercooling studies[12] on Al-based alloys. Quantitative studies are required, however, taking account of possible diffusion effects during nucleation [13] and using accurate measurements of the driving free energies and atomic mobilities.

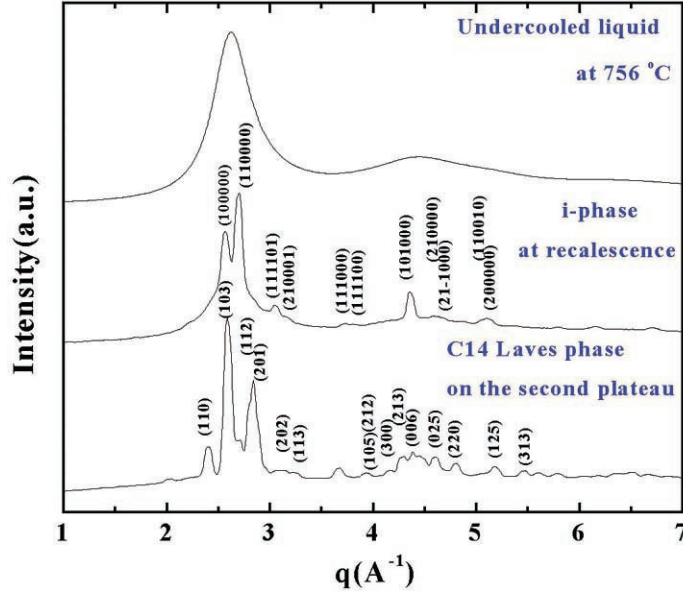


Fig. 4. In-situ x-ray diffraction showing the nucleation and growth of the i-phase and its subsequent decomposition to the C14 Laves phase during recalescence.

3.3 Liquid Specific Heat Measurements

A knowledge of the specific heat at constant pressure for the undercooled liquid, C_p^l , and the various solid phases is essential to the success of the proposed benchmark nucleation experiments on the ISS. An accurate analysis of the nucleation data requires that the driving free energy $\Delta G_v(T)$ be computed from the measured enthalpy of fusion at the melting temperature, ΔH_f and the specific heat difference between the liquid and the solid phases, $\Delta C_p^{l,s} = C_p^l - C_p^s$,

$$\Delta G_v = \frac{\Delta H_f \Delta T}{T_m} - \int_{T_m}^T \Delta C_p^{l,s}(T') dT' + T \int_{T_m}^T \frac{\Delta C_p^{l,s}(T')}{T'} dT' \quad (1)$$

where ΔT is the amount of undercooling ($T_m - T$). Unfortunately, few experimental data are available for ΔH_f and $\Delta C_p^{l,s}$, especially, for alloys and compounds with high melting temperatures. In the absence of experimental data, many workers have used approximate expression for $\Delta G_v(T)$ [3]. However, no single expression is universally acceptable for different alloys. Further, the analysis of nucleation data with these approximate expressions often leads to orders of magnitude error in the estimated nucleation parameters[3, 14].

Because of the high vacuum and containerless processing capability, ESL is particularly suitable for specific heat measurements in the liquid and undercooled state for high temperature alloys, if the sample emissivity is known. In the ESL, the levitated sample cools freely by radiation loss. For a sample of radius, r , and emissivity, ϵ , the rate of heat loss at temperature T is given by the Stefan-Boltzmann relation,

$$H = 4\pi r^2 \sigma \epsilon (T^4 - T_o^4), \quad (2)$$

where k is the Stefan-Boltzmann constant, and T_o is the surrounding temperature. Balancing this heat loss with the cooling rate (dT/dt) for a sample of mass m , and specific heat C_p^l , one obtains

$$m C_p^l \left(\frac{dT}{dt} \right) = 4\pi r^2 \sigma \epsilon (T^4 - T_o^4) \quad (3)$$

By measuring the cooling for a sample of known radius, mass, and emissivity, the specific heat can be calculated from Eq. (3). Unfortunately, ε is known only for a few elements and alloys such as, Ni, Zr, and $\text{Zr}_{75}\text{Ni}_{25}$ [15] over a limited spectral and temperature range. Therefore, ε was estimated either by extrapolating the data for $\text{Zr}_{75}\text{Ni}_{25}$ to the pyrometer wavelength used in the present investigation (1.2 – 1.4 μm), or by adjusting its value to match the known melting temperatures of binary alloys. Both methods gave $\varepsilon = 0.25$ for the Ti-Zr-Ni alloys for the wavelength range used. Any temperature dependence for ε was ignored, because it changes only by one to two percent between 1000 and 1500 K for pure Zr and a related binary $\text{Zr}_{75}\text{Ni}_{25}$ alloy[15].

The C_p^l for a large number of ternary Ti-Zr-Ni alloys in the liquid and undercooled state were determined from the free-cooling data. Fig. 5 shows the C_p^l data for a few representative compositions containing equal Ti and Zr and increasing Ni, which crystallize first into the $\beta(\text{Ti/Zr})$ phase. The most important trend is an increase in C_p^l as well as its temperature dependence with increasing Ni. In Fig. 6, the specific heat of Ti-Zr-Ni alloys containing higher Ni (21 at.% $\leq$ Ni $\leq$ 30 at.%) are shown. As pointed out in §3.2, the primary nucleating phase for the 21 at.% Ni alloy is the i-phase; it is the C14 Laves for the other compositions. The trend of an increase in C_p^l with increasing Ni is similar to that observed for the $\beta(\text{Ti/Zr})$ phase forming alloys. The important difference is that C_p^l goes through a maximum in the undercooled state. After careful consideration to all possible sources of error, we concluded that this is not an

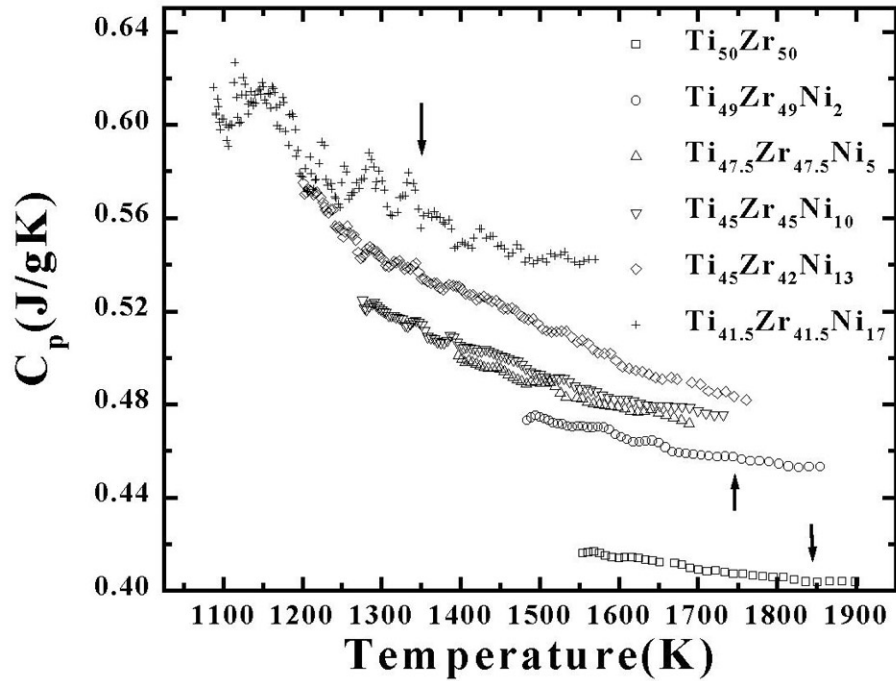


Fig. 5. Specific heat as a function of increasing Ni for alloys with equal concentration of Ti and Zr. Arrows indicate the liquidus temperatures.

experimental artifact. Further, no anomalous change in the liquid structures measured by BESL was observed in this temperature range that would suggest a phase separation in the undercooled liquid. Interestingly, Sommer found[16] that in ternary $\text{Al}_2\text{La}_3\text{Ni}_3$, C_p^l above T_g is smaller than at the liquidus temperature, although C_p^l increased with decreasing temperature, implying the existence of a maximum in C_p^l between T_g and the liquidus temperature. However, data in the intermediate temperature range

were not available to confirm this. This is the first known alloy system that shows a maximum in C_p^l . Sommer[16] tried to explain the possible maximum in C_p^l of $\text{Al}_{30}\text{La}_{50}\text{Ni}_{20}$ in terms of a competition between the chemical short-range order (CSRO) in the liquid binary alloy (Al_2Ni) and the CSRO in the ternary liquid phase ($\text{Al}_2\text{La}_3\text{Ni}_3$). To quantitatively apply this model to our data, more information on clusters present in the liquid is necessary. Qualitatively, however, the maximum in C_p^l should be related to a changing viscosity in the melt. The maximum should occur somewhere near T_g , where the viscosity rises rapidly. In contrast, the present maximum occurs around $0.05\text{-}0.06T_m$. Interestingly, some recent molecular dynamics calculations[17] predicted a maximum in C_p^l , if the liquid changes its character from fragile to strong. Work is in progress to check this possibility in the present system. Also, modulated calorimetry measurements, possible in MSL-EML, are needed to confirm this peak in the specific heat.

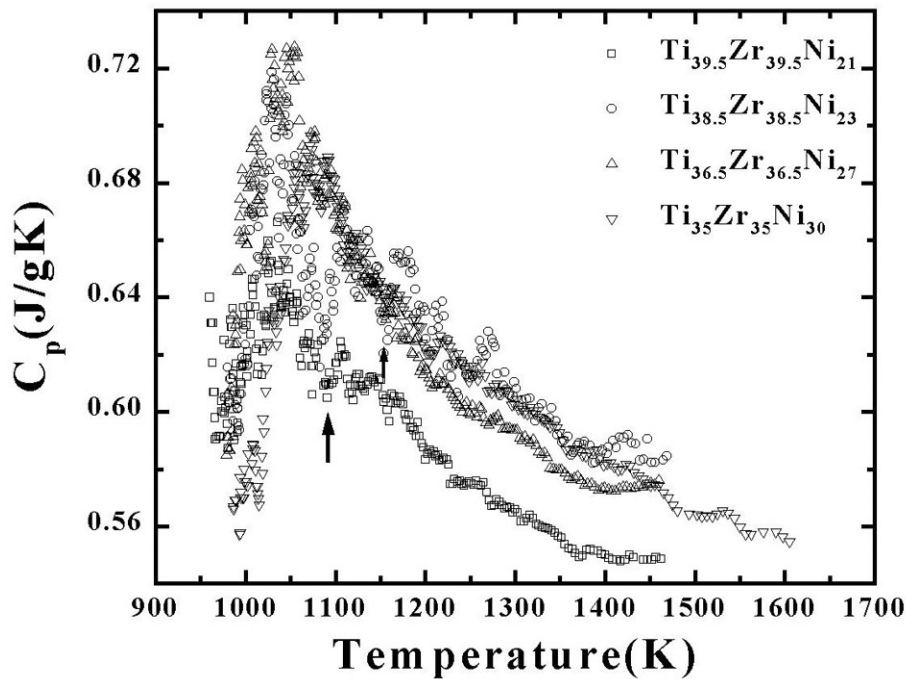


Fig. 6. Specific heat of Ti-Zr-Ni alloys containing higher Ni and equal Ti and Zr. Arrows indicate the liquidus temperatures of the corresponding compositions.

3.4 Viscosity and Surface Tension Measurements

A knowledge of the diffusion coefficient, D , in the undercooled liquid is essential for a detailed modeling of the nucleation of crystalline phases from the undercooled liquid[3]. In addition, viscosity can also provide important information on the short-range order of the undercooled liquid and show indications of a possible fragile to strong phase transition. Since the measurement of D is difficult and time consuming, especially for multi-component alloys where a knowledge of the diffusivity of each atomic species is preferred, D is, often, estimated from the viscosity (η) using the Stokes-Einstein relation ($D = kT/3\pi a\eta$, where k is the Boltzmann constant, T is the temperature, and the parameter a is of the order of the covalent radius). Although surface tension data are not necessary for nucleation studies, they are needed to estimate the surface-driven convection (Marangoni flow) during the droplet processing to assess the role of convective flow and diffusive flow on nonpolymorphic nucleation processes under terrestrial or microgravity conditions. The surface tension data are obtained naturally, if the viscosity is measured by the droplet oscillation technique.

The viscosity and surface tension of a liquid can be measured by observing the effects of induced oscillations in a droplet. If the radius, R , of a liquid drop undergoes surface oscillation of the form,

$$R = R_0(1 + \delta \cos(\omega t)e^{-\lambda t}), \quad (4)$$

where δ is the amplitude, ω is the frequency, and λ is the damping constant of the oscillations, the frequency is related to the surface tension σ and the sample mass m by Rayleigh's formula,

$$\omega^2 = (32\pi\sigma)/(3m), \quad (5)$$

The damping constant λ is related to the viscosity η by Kelvin's formula,

$$\lambda = (20\pi\eta R_0)/(3m), \quad (6)$$

Measurement of the oscillation frequency, the damping constant, and the sample radius and mass can, therefore, be used to calculate the surface tension and viscosity of the liquid. Oscillations on a contamination- and distortion-free droplet are a necessary prerequisite for the success of this technique. This necessitates containerless processing (EML or ESL), preferably under microgravity[18, 19].

The viscosity of the i-phase forming composition $\text{Ti}_{37}\text{Zr}_{42}\text{Ni}_{21}$ was measured, both in the liquid and undercooled state before the onset of crystallization, using the ESL facility at MSFC, Huntsville. The viscosity data are shown in a semi-logarithmic plot in Fig. 7. The activation energy calculated from the slope of the straight line is 61 KJ/mol. This value is much higher than in transition metals (50.2 KJ/mol for Ni and 41.4 KJ/mol for Fe[20]), suggesting the formation of a network of clusters in the liquid. The

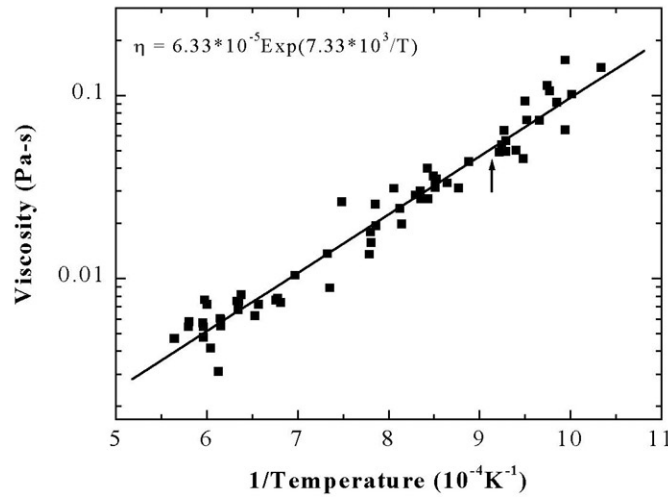


Fig. 7. Semi-logarithmic plot of the temperature dependence of viscosity of $\text{Ti}_{37}\text{Zr}_{42}\text{Ni}_{21}$ alloy in the liquid and undercooled state.

smooth extrapolation of the data from the liquid to the undercooled state, however, shows no abrupt change in the short-range order of the liquid below the liquidus temperature (marked by an arrow). Interestingly, this is the first measurement of viscosity of any Ti-Zr-Ni alloy in the liquid and undercooled state. Measurements of other compositions which nucleate $\beta(\text{Ti/Zr})$ (low Ni) and the C14 Laves phase (27 at.% < Ni < 33 at.%) are in progress.

4. Conclusions

From extensive ground based work on the phase diagram and undercooling studies of Ti-Zr-Ni alloys, we have clearly identified the composition of three different phases with progressively increasing polytetrahedral order such as, β (Ti/Zr), the C14 Laves phase, and the i-phase, that nucleate directly from the undercooled liquid. The reduced undercooling decreases progressively with increasing polytetrahedral order in the solid, supporting Frank's hypothesis[4]. A new facility for direct measurements of the structures and phase transitions in undercooled liquids (BESL) was developed and has provided direct proof of the primary nucleation of a metastable icosahedral phase in some Ti-Zr-Ni alloys. The first measurements of specific heat and viscosity in the undercooled liquid of this alloy system have been completed. Other than the importance of thermo-physical properties for modeling nucleation and growth processes in these materials, these studies have also revealed some interesting new results (such as a maximum of C_p^l in the undercooled state). These ground-based results have clearly established the necessary background and the need for conducting *benchmark* nucleation experiments at the ISS on this alloy system.

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MONODISPERSE LIGAND STABILIZED GOLD NANOPARTICLES. UNDERSTANDING THE EFFECTS OF DIFFERENT LIGANDS.

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It is proposed that new types of crystalline materials could be grown in perfect shapes in microgravity. Especially promising are nanocrystal superlattices (NCSLs) based on gold, since gold is heavy and can readily be prepared in ligand stabilized nanocrystalline form. However in order to bring this idea to fruition better synthetic methods for preparing large amounts of cleanly monodisperse gold nanocrystals must be devised. This led to the discovery of a digestive ripening process. Indeed, we have found that heating a metal containing colloid at or near the solvent boiling point in the presence of a surface active ligand, is an extremely efficient procedure to prepare highly monodisperse colloids. This process has been called digestive ripening, and the usefulness of thiols as digestive ripening agents has already been established. In an effort to find alternative digestive ripening agents we have now used alkyl- amines, silanes, phosphines and halides. Amines and silanes were found to be similarly efficient for this purpose. The important steps involved in the digestive ripening have been identified as i) breaking the polydisperse colloid into a much smaller nanoparticles, ii) isolating these smaller particles from reaction side products, and iii) refluxing the isolated small nanoparticles in the presence of the ligand. The success of a ligand as a good digestive ripening agent is based on its capacity to break the bigger nanoparticles into smaller ones in the first step and its ability to adhere to the nanoparticle surface while the reaction side products are being removed in the second step. Though most of the ligands do a reasonably good job in the first step, some fail in the second step rendering them ineffective as digestive ripening agents. The similarities between the successful digestive ripening ligands will be discussed in detail. It was also found that irrespective of the head group, ligands with shorter alkyl chain lengths favor 3D ordering of the resulting monodisperse colloids while those with longer alkyl chain lengths lead to 2D lattices. The reasons for this are explained based on the decreasing van der Waals attraction between the gold particles as the distance between them is increased through the alkyl chain length of the capping ligand.

Keywords: nanocrystal superlattice, microgravity, ripening, monodisperse, ligand, gold, nanostructures

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DATA AND MODELING OF DENDRITES SUBJECT TO A STEP CHANGE IN PRESSURE (TDSE)

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There is considerable interest in dendritic solidification because of the influence dendrites have in the determination of microstructure, and thereby in the physical properties of cast metals and alloys. Current theories and models of dendritic growth generally couple diffusion effects in the melt with the physics of the interface. Data and subsequent analysis prior of the tip growth speed and radii of thermal succinonitrile dendrites in the near-convection free, on-orbit, free-fall environment demonstrate that these theories yield predictions that are reasonably in agreement with the results of experiment. However, data and analysis for assessing the interfacial physics component of theory are not sufficiently detailed or definitive. To study fundamental aspects of dendritic interface stability, we are measuring and modeling the kinetics and morphology of dendrites as they evolve from one well-defined steady state at a pre-set supercooling, through a transient stage, to a different well-defined steady state.

More specifically, we subject succinonitrile dendrites, growing under steady-state conditions, to a rapid change in pressure. This leads to a rapid change in thermal driving force from the corresponding change in both the equilibrium melting temperature due to the Clapeyron effect, and a change in the far-field temperature due to adiabatic temperature changes in the bulk liquid and solid. Subsequently, we observe transformations from a well-characterized initial state into a new steady-state. Initial data reveal that the dendrite tip velocity changes almost as fast as the pressure charges, while the tip radius changes occur more slowly, taking from 10 – 60 seconds depending on the size of the step change and the final supercooling. Computer modeling of this process shows both agreements and disagreements with the experimental data. In making these observations and measurements, we are gaining new understandings of interfacial dynamics and state-selection physics.

Introduction

Dendritic solidification is one of the simplest examples of pattern formation where a structureless melt evolves into a complex crystalline microstructure. Dendrites are known to occur in the solidification of water, salts, organic materials, and most commonly and importantly, in metals and alloys. There is considerable engineering interest in dendrites because of the role dendrites play in the determination of the physical properties of cast materials. In addition, dendritic solidification has become a well-studied model in the fields of non-equilibrium physics, and computational condensed matter material physics [1].

Keywords: dendrite, solidification, microstructure, interfacial, Clapeyron, flight

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Current theories of dendrite formation contain two independent components. The first concerns the transport of heat and solute from the solid-liquid interface into the melt. The second involves the interfacial physics that selects the unique growth velocity and tip radius of curvature from a spectrum of possibilities that are all consistent with the heat transport and conservation of energy at the crystal-melt interface. Until recently, neither aspect of the theory could be tested critically because of the effects of gravity-induced convection, which modifies the transport processes, and alters the growth kinetics [2].

To circumvent this difficulty, benchmark data were obtained in microgravity during two flights of the Isothermal Dendritic Growth Experiment (IDGE), using succinonitrile (SCN) as the test material [3, 4]. SCN is an organic material that acts as a BCC metal analog. The data and subsequent analysis of the dendritic tip growth speed and radii of curvature for these SCN dendrites demonstrated that although the theory yields predictions that are in reasonable agreement with the experiment, several significant discrepancies occur. However, some of the discrepancies can be understood by a consideration of the diffusion of heat from three-dimensional dendritic structures [5, 6]. The data and analysis for assessing the pattern selection physics are less definitive.

Current investigations by other researchers are studying, isolated single dendrites, dendritic side-branching, aligned dendritic arrays, and equiaxed dendritic growth. Some of these investigations recognize that in addition to the study of steady-state growth features, where the tip region of the dendrite grows at a constant speed, dendrites also exhibit time-dependent, non-steady features. For example, time-dependent side-branches emerge, amplify, and eventually coarsen.

The work presented here represents preliminary results from our activities to study fundamental aspects of time-dependent dendritic growth, while retaining the advantages of working with a single, isolated dendrite.

We are investigating transient and time-dependent dendritic growth by employing the relatively large Clapeyron effect in SCN with pressure changes. A rapid change in a solidifying system's hydrostatic pressure quickly changes the liquidus temperature, and induces a change in the temperature gradients at the interface. With this approach, we have observed and measured the kinetics of isolated dendrites as they evolves from one well-defined steady-state velocity, at a pre-set supercooling, through a transient stage, to a new well-defined steady-state velocity at the altered pressure-supercooling state.

Background

A major challenge in measuring and analyzing the transient behavior of isothermal dendrites growing from an initial nucleus is defining precisely the initial conditions from which the dendrite evolves. The experiment described in this paper obviates this difficulty, because the transient instead occurs between two well-characterized steady states—controlled by pressure, rather than between an ill-defined initial state and the final steady state.

The definition of the melting temperature, T_m , is the temperature at which the liquid and solid phases co-exist in equilibrium. The melting temperature of a pure material has a well-established value, which varies as a function of pressure. In materials that expand on melting (well known exceptions being water and silicon), pressure favors the solid phase as atoms or molecules are squeezed (on average), slightly closer together. The increase in pressure does work on the solid, decreasing bond lengths, and raising the melting temperature. This effect is classical, and can be derived from general thermodynamic principles yielding

the Clapeyron equation,

$$\frac{\Delta T}{\Delta P} = \frac{T_m(v_l - v_s)}{h_f} \quad (1)$$

where ΔT is the change in melting temperature resulting from a change in pressure, ΔP , and v_l and v_s are the specific volumes of the liquid and solid phases, and h_f is the latent heat [7]. We measured directly the Clapeyron effect in high-purity SCN by two independent techniques and determined that $\Delta T/\Delta P = 24.5 \pm 0.5$ mK/atm [8].

The Clapeyron effect is well known in solidification theory and has been hypothesized as the explanation for cavitation induced nucleation. However, it is usually assumed that the Clapeyron effect is too small to be of interest in the solidification of metals and alloys. This is a reasonable assumption for most materials, but not valid in the unusual case of SCN, which has a Clapeyron effect that is many times larger than most metals and a unit supercooling that is many times smaller. Thus, the ratio of the Clapeyron Effect to the Unit Supercooling is 25 to 200 times larger for SCN than for typical metals. This indicates that pressure effects can be important in the solidification of SCN (at least for the purpose of conducting basic research).

The Clapeyron coefficient of 24.5 mK/atm can be used in a straightforward manner to quickly change a crystal-melt interface's equilibrium melting temperature, and, thereby, its supercooling. If this is done for an isolated isothermal dendrite growing at steady state, the supercooling, and the associated free energy for dendritic growth, becomes instantaneously and globally altered. This approach, allows acquisition of a series of unique measurements of non-steady-state dendritic kinetics, and permits observations of the transient evolution of the morphology.

If a pressure-mediated melting temperature change is carried out for an isolated dendrite growing at steady state under some initial supercooling, the dendrite needs to respond by eventually adopting a new steady-state that is appropriate to the new supercooling. If we designate in advance a particular target supercooling, we can achieve that supercooling by starting at a supercooling either above or below that supercooling, and then apply upward or downward pressure quenching as needed. To properly calculate what that final supercooling is, one must account for the influence of the adiabatic pressure-volume work done on the melt. From the thermodynamics of the combined first and second laws, one can show that the change in the melt temperature (or similarly, crystal temperature) with pressure is,

$$\frac{\Delta T}{\Delta P} = \frac{\beta v T}{c_p} \quad (2)$$

where β is the isothermal compressibility, v is the specific volume, T is the temperature of the melt prior to the pressurization, and c_p is the constant pressure specific heat. For SCN, this is approximately 13 mK/atm, confirmed by both calculation and direct measurement.

Experiment Description

The experiments described here were conducted using ground-based hardware originally produced and used by the Isothermal Dendritic Growth Experiment (IDGE) to study dendritic growth of succinonitrile and pivalic acid under both ground and microgravity conditions. Additional detailed information describing the IDGE can be found elsewhere [9, 10].

Apparatus

The experimental apparatus is centered about the sample material, contained by a stainless steel growth chamber located within a temperature-controlled bath. The growth chamber interior volume communicates with the bath via a stainless steel bellows, permitting the pressure in the bath to be transmitted into the chamber interior. Nucleation of dendritic crystals was achieved through the use of a hollow stinger tube that penetrated the wall of the growth chamber. The exterior end of the stinger tube was capped and surrounded by a thermoelectric cooler. The interior end was open, allowing the sample material in the chamber to also fill the stinger.

During the operation of the experiment, each dendritic growth cycle began by completely melting the SCN, followed by lowering the melt's temperature to the desired supercooling. After the supercooled melt's temperature reached steady state, the thermoelectric cooler was activated. This nucleated a small crystal in the end of the stinger, which then propagated down the stinger tube to emerge into the chamber as a freely growing dendrite. Upon reaching steady state growth, the hydrostatic pressure of the surrounding thermal bath was changed via a pneumatically operated piston. This pressure was transmitted to the sample via the bellows, causing a change in the operating state of the dendrite. From here, the dendrite was observed as it attempted to acquire a new set of steady state operating conditions. Once one of these "growth cycles" was completed, a new growth cycle was initiated by re-melting the sample and proceeding as described above. This arrangement produced dendritic crystals grown with the bath steady state temperature controlled to within 0.002 K (spatially and temporally).

During the growth cycles, once a crystal emerged from the stinger, images of the dendrites were obtained from two perpendicular views using electronic cameras which provided the spatial and temporal resolution that is necessary to study the transient aspects of the growth process. Specifically, an imaging chip array was used of 640 x 480 pixels (256 gray-scale levels) and an imaging rate of approximately 30 frames per second (~30 Hz).

Analysis Techniques

The data presented here from the 30fps video cameras has an optical resolution that related to the base size of an individual pixel in the video camera's imaging array. Each pixel, after correcting for the magnification of the optics system, images a region of the growth chamber that is approximately 22 mm high and 22 mm wide. This value constitutes the raw measurement precision for the tip position data. It is necessary to improve upon this precision by applying a sub-pixel resolution image analysis method to each image in the growth cycle.

The method used for the data presented here begins by examining the first and last image frames of a growth cycle. The dendrite tips are found in these images using a row-by-row search to locate the lowest pixel in the field of view that is darker than a specified threshold value. If there are more than one pixel in a row satisfying this criteria, an average is calculated to obtain the horizontal coordinate. With these crude estimates of the tip positions at the beginning and end of the growth, it is possible to construct a vector that can be used to predict where the tip will be in all frames during the growth, provided the frame number and frame rate are incorporated. This tip-location prediction scheme improves processing efficiency, though is only capable of resolving information on the order of 22 microns (one pixel).

Using this predicted tip location, a second stage of refinement is added to the sub-pixel interpolation processing of each image. This is achieved by overlaying a “sampling line” along the predicted vector and determining the point along this vector where the image intensity crosses a selected threshold value. However, the sampling line is treated as “thick” in that it also comprises of several pixels on either side of the mathematical line, creating an averaging effect. Additionally, interpolation is applied to determine the threshold location more precisely. By incorporating a statistically larger number of pixels in this second stage of refinement, resolution is improved to approximately 7 microns ($\sim 1/3$ pixel). However, the horizontal coordinate is constrained to fall along the predicted vector line. In practice, this is not usually a significant issue, since these dendrites tended to grow within about 10 degrees of vertical, and, once started, do not deviate in direction under nominal growth conditions.

The final stage of resolution enhancement is achieved by a somewhat unorthodox approach, which has the advantage of incorporating still more (statistically speaking) information concerning the tip location. Figure 3 shows a typical image of a dendrite tip (video image in 3b). Using the refined tip location (stage 2, described above) as a reference location, a box is created around the tip. Next, the centroid of the pixel intensity within this box is calculated. In practice, the coordinates of this centroid exhibit a resolution of approximately 2 microns ($\sim 1/10$ pixel). This approach doesn’t actually locate the tip’s interface. Instead, it uses more data to obtain a more consistent reference point, which serves to track the tip’s movement over time. The size of the sampling box used in the centroid calculation is somewhat arbitrary. The concerns in its selection are primarily over obtaining a balance between the desire to have a large number of data points contributing to the measurement, and avoiding the inclusion of side branches. When information that is obtained from regions further removed from the tip is used, nascent side branches can contribute to the centroid calculation in a periodic manner.

Once extracted from the images, the tip positions are then converted into a displacement vs. time data set that is used for subsequent analysis. The displacement is calculated relative to the tip position in the first available frame of video [9]. The radii measurements are based on 35 mm film following the procedures described in reference [4]. However, at this point the details of the optic system have not been tailored to produce the best quality images, and thus the uncertainties in these measurements are larger than those quoted in reference [4].

Results

The experiments described above were conducted for a variety of pressure change magnitudes and directions, and with a variety of supercooling levels. What follows is a qualitative survey of typical observations.

An increase in hydrostatic pressure is expected to result in an increase in the interface’s equilibrium temperature, and thus an increase in the temperature gradient and supercooling which drives the solidification process. Figure 1 plots the dendrite tip displacement vs. time of such an experiment. The velocity of this growth (i.e. the slope) is indeed observed to increase after the pressure change, confirming the general feasibility of the experimental procedure. Earlier we reported in the transition from an initial low velocity to a final higher velocity, that the dendrite had a short transient where it initially slowed [11]. That report however was in error as the observed short initial transient was due to an instrument error.

When the melt's hydrostatic pressure was instead decreased during the growth, as expected, the growth rate also decreased.

The tip position data (as a function of time) is the primary measured data in these experiments. It is desirable to convert this information into the dendrite tip growth velocity. Due to the point-by-point variability of these measurements, instantaneous measures of the velocity are best interpreted when they incorporate some form of moving average or data smoothing. However, for the data reported here, the correction to account for the instrumental error added so much noise that a velocity plot is not useful, even using a moving average. Nevertheless, we compare the experimental data to the modeling data modeling with respect to the velocity versus time rendering of the data.

For the range of supercoolings and pressure change magnitudes, the characteristic time necessary to reacquire the new steady-state velocity was too similar to the pressure transition time to be seen as independent of the pressure transition. The best that we can say is that it must be on the order of 0.2 s or less.

When we began these measurements, we had no estimate of the time scale involved for the dendrite to respond to a change in its conditions. In the case of velocity measurements, low spatial resolution data at 30 fps was more than adequate to see, recognize, and perform preliminary analysis on the velocity changes that occurred. These observations were reported above.

Assessing the response of the tip radii of curvature (i.e., the tip size) is a more difficult task, as the number of photographs, the time between photographs, and the optical quality of the images were not well tailored for quantifying the radius changes that occurred. This was particularly the case for dendrites grown at larger supercoolings and with smaller supercooling steps.

Despite these challenges, we did obtain sufficient data to verify the basic concept and approach, and to know how to set the parameters for future improvements in data acquisition. Based on a first sampling, we believe that the initial and final radii are different enough (under these conditions) to be measurable.

When measurable, the transient phase of R transpires in an exponential manner (at least for the larger tips with larger ΔT_{step}). Lastly, the duration of the transient appears to be a function of supercooling where the transition time ΔR is longer at lower ΔT_{mean} .

Additional higher quality data would enable us to measure how the interface shape evolves during the transient phase. We have no reason to expect that it will retain the same shape during the transition. In addition, the transient period as a function of ΔT_{step} and ΔT_{mean} should be measurable. For some growths, though not all, the transient is clearly identifiable and appears to be completed within the period of data acquisition, even when crudely measured using the initial data.

Simulations

The data presented here demonstrate the effectiveness of using pressure changes to influence the process of dendritic crystal growth. Here, we describe the results obtained from numerical simulations of the governing equations for heat transport during solidification of SCN. Our simulations start from an initially small spherical nucleus of supercritical size (i.e., unstable with respect to perturbations), onto which we

add small random perturbations. The equation is the heat conduction equation, which is solved in both the liquid and solid phases.

The simulation is performed in a finite domain, where the external boundary is at any desired location and with a prescribed temperature that could arbitrarily be set to any value at any time during the simulation. The time-dependent calculations were performed using finite difference techniques and using the Triad Field Formalism (Pines et. al [12]). In this technique, the governing equations are mapped using three fields onto a fixed computational domain. The location of the dynamically evolving interface is solved as a part of the solution. The code uses highly efficient operator splitting techniques with arbitrary precision. The code was previously used and extensively tested against analytical results (where available) and experimental data from the IDGE experiment. The code incorporates adiabatic temperature changes and the Clapeyron effect for application to the TDSE research program.

We have explored several key features of the solution obtained from the numerical simulations of the experiment. We begin by imposing a pressurization/de-pressurization cycle of ca. 265 psi, with a time constant for the exponential pressure changes of 2 seconds. The supercooling was set to approximately 0.1 K. For this simulation, the tip position vs. time behaves similarly to the experimental data discussed previously.

It is evident that pressurization produces a faster tip velocity. An interesting feature is that the tip velocity changes to a higher value quickly at first, then decreases slightly, after which it slowly evolves to a final steady state. Additionally, there is a decrease in tip velocity upon de-pressurization. The down-pressurization does exhibit the slight over-response as did the up-pressurization, but then rapidly achieves its final steady state. The radius of curvature at the tip transitions is in accord with the supercooling conditions, but as seen experimentally, the change occurs even more slowly than the tip velocity. It is important to note that both the V and R values are in reasonable agreement with the experimental values from IDGE for the same level of supercooling. Additionally it should be noted that simulations performed starting with different random small perturbations always result in the same final steady values of R and V .

Discussion

Of interest are the hysteresis measured in the simulated values of V and R following the pressurization and de-pressurization cycle, and the lack of hysteresis in the Péclet number. Comparable experiments have not yet been performed, and thus we are not yet able to evaluate this simulation result, and may not until we can perform the appropriate experiments in a convection-free environment. In addition, the simulation although in agreement with some of the experimental data, is in disagreement with other experimental observations. Further analysis of these comparisons provides an opportunity to identify either aspects of the experimental configuration that are not being modeled, or aspects of solidification that are not being modeled.

We see additional agreements and disagreements when we compare both the triad field formulation simulation and the experimental data to phase field models of dendritic growth of liquid crystals subject to pressure changes [13].

Future Efforts

The preliminary observations and comparisons that have been presented here demonstrate that there is much more to be learned by studying pressure-mediated dendritic growth. In reaching this end,

experiments are being planned which will incorporate larger changes in supercooling (pressure), a wider range of average supercoolings, measurements of the characteristic length scales (tip radius of curvature), side branching characteristics, the influence of convection, and the process of single dendrite coarsening.

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STRUCTURE PROPERTY CORRELATIONS AND PHASE TRANSITIONS IN GROUP IV AND III-V LIQUIDS

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Introduction

Prior molecular dynamics (MD) simulations and laser pulse-heating studies on amorphous Si indicate that Si, Ge, and III-V liquids may undergo a first-order liquid-liquid phase transition [1-3]. For Si and Ge, this transition is predicted in the deeply supercooled liquid. Group III-V and SiGe alloy liquids are expected to exhibit the transition closer to their respective melting temperatures. The MD simulations predict that the transition occurs from the metallic liquid to a tetrahedrally-coordinated, viscous and semiconducting liquid. The models also predict a decreasing coordination of Si atoms as the liquid is supercooled towards the transition temperature. However, no direct experimental characterization of the low-coordination phases has been obtained. The purpose of this ground-based research program is to: (1) search for and independently confirm the existence of such first-order transitions, and (2) determine the liquid phase structures.

This experimental research program is based on the use of conical nozzle levitation techniques to study the supercooled liquid phases, combined with x-ray diffraction experiments to investigate structural changes in the liquid. The structural results were obtained in four experimental campaigns at the Advanced Photon Source (APS) using the synchrotron x-ray source. Total and partial x-ray structure factors were obtained as a function of temperature and composition over a wide range of Q (momentum transfer) for liquids in the normal and supercooled states. The range of materials studied include silicon, Si-Ge alloys, GaSb, and InSb, YAG, and a number of materials of interest to other NASA PIs. At this conference, results will be present new results on liquid Si, Si-Ge alloys, and GaSb alloys.

The present study builds on prior work on liquid Si performed by our research group [4,5] in which we first showed that the first shell coordination and nearest neighbor distances for liquid Si decreased with increased supercooling. This new study builds on this prior finding through measurements at high supercoolings and on SiGe liquids.

Experimental

This work was performed with the combination of conical nozzle levitation (CNL) techniques on laser-heated liquids and synchrotron x-ray diffraction. The experimental hardware and techniques used for the present study follow previous experimental campaigns at the Advanced Photon Source (APS). Previous papers on YAG and Mullite [6,7], and a recent review article [8] provide detailed descriptions of the experimental methods and data analysis procedures employed in our previous study on silicon. A brief summary and key modifications to the apparatus are discussed below.

Keywords: liquid silicon, phase transitions, x-ray diffraction, supercooling, characterization

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The conical nozzle levitation apparatus was used to position the specimens at the center of a Huber six-circle X-ray diffractometer at the beamline 12-ID-B at the National Synchrotron Light Source. The levitation system was enclosed in an environmentally-controlled chamber equipped with Be windows for transmission of the incident and scattered X-rays. The chamber included several ports that provided access for optical pyrometry, video imaging and laser beam heating of the specimens. Most experiments were conducted at a chamber pressure of 600 mBar, with a levitation gas flow rate of about 350 cm³/min of pure argon. A key modification to the apparatus was the use of a titanium-getter furnace to further purify the incoming gas; the oxygen and nitrogen content of the gas was estimated to be < 0.01 ppm.

A 270-W CO₂ laser was employed as the heat source to achieve liquid temperatures in the range 1200-1800K for Si and SiGe. Another modification to the apparatus was to include a second CO₂ laser (40-watts of laser power) to provide additional heating of the specimen from below through the opening in the nozzle. At the lowest specimen temperatures, the power delivered to the specimen from below was roughly equal to the power delivered from above. This was the key factor in being able to achieve high levels of supercooling on liquid Si. In the absence of this lower-side heating, the bottom of the specimen would be considerably colder than the top and high supercoolings would not be achieved.

Specimen temperatures were measured using two different pyrometers with operating wavelengths of 0.65μm and 2.0μm and emissivity corrections were applied based on the previous measurements of Krishnan, *et al* [9]. A spectral emissivity of 0.30 at 0.65μm was assumed for liquid SiGe. During a given experiment, temperature fluctuations on the order of 5K were observed. Specimens were maintained at each temperature for a duration of up to 60 minutes in order to achieve high statistics in the x-ray measurements.

All X-ray measurements were obtained using a monochromatic beam in the energy range 20-30 KeV. Scattered X-rays were detected using a solid-state detector with 300 eV resolution over a 2θ angular range of 2-110°. X-ray diffraction data were obtained on liquid Si in the angular momentum transfer range (Q) of 0.8 to 21 Å⁻¹. The X-ray background and attenuation of the incident X-rays by the ambient gas at the operating pressure in the experiment chamber was independently measured without a specimen.

Data analysis for Si and SiGe

The data analysis methods used in the present work differ from that employed in our prior study on liquid Si [4,5]. The air scattering was removed from the scattered intensity, using a fitted Lorentzian shape. The multiple scattering also contributes to the background radiation for a few percent and this contribution was eliminated analytically using the procedure of Warren and Mozzi [10]. The atomic scattering factors were calculated using values from Wassmaier and Kirfel [11] and the anomalous dispersion was taken from the Henke [12] tables. The coherent scattered intensity was extracted from the experimental measurements using the method of Wagner [13]. Following this formalism, the x-ray intensity $I_s(Q)$ scattered by the sample and corrected for air scattering and multiple scattering is given by:

$$\frac{I_s(Q)}{I_0(Q)} = A_{coh}(Q)I_{coh}(Q) + A_{incoh}(Q)I_{incoh}(Q) \quad (1)$$

where $I_0(Q)$ is the intensity of the incident beam measured with an ionization chamber, A_{coh} and A_{incoh} are attenuation terms for the coherent and incoherent scattered intensities I_{coh} and I_{incoh} . The attenuation coefficients were determined using numerical integration of the optical path of the x-ray beam over the irradiated volume of the sample. For this calculation step, absorption coefficients were approximated by

the x-ray cross sections compiled by McMaster *et al* [14]. Finally, the incoherent scattering intensity was calculated using data from Balyusi [15].

The pair correlation function $g(r)$ was obtained by a classical Fourier transform of $S(Q)$. The number density was taken as $0.0493 \text{ atom}/\text{\AA}^3$, based on the known mass density of 2.5 g/cm^3 . A number density of 0.0275 was used for liquid SiGe based on an extrapolation of mass densities.

Results

Figure 1 is the X-ray weighted average structure factor, $S(Q)$ obtained in the present study for liquid Si in the temperature range 1767-1434K; the bottom curve corresponds to the highest temperature while the top curve corresponds to the lowest temperature at which X-ray measurements were obtained. The latter represents a supercooling of roughly 254K. The other two curves at 1667 and 1543K also correspond to measurements in the supercooled region.

The significant result in these newer measurements is the rather excellent statistics, the sharp definition of the key features in the $S(Q)$, and the wide Q -range. The shoulder observed on the high- Q side of the first peak is very well defined, and this appears to sharpen considerably with supercooling. A similar result was previously observed by Ansell, *et al* [4] and by Kimura, *et al* [16] with increased supercooling. Additionally, there is excellent definition of the first three peaks in the $S(Q)$, but there is rapid damping of the structure at higher Q . In addition, the shoulder on the high-side of the first peak for the deeply supercooled liquid does not appear to be a shoulder; rather it appears to define a peak in the $S(Q)$. Such a sharp definition has not been seen in previous x-ray investigations, although the general sharpening of the shoulder with supercooling has been noted.

Pair correlation functions $g(r)$ were obtained by a direct Fourier transform of the $S(Q)$; the rather large Q -range and the high statistics of the experiment produced excellent $g(r)$ results as can be seen in Fig. 2. The $g(r)$ is characterized by three well-defined peaks at roughly 2.46, 3.9, and 5.7Å. The first nearest neighbor distance over the full temperature range is around 2.48Å, with no real trend with temperature. This result differs from the earlier result of Ansell, *et al* [4], and is similar to the results reported by Kimura, *et al* [16]; the differences between the current results and those of Ansell, *et al* [4] are believed to be due to the much larger Q -range of the current study that tends to yield pair correlation functions with slightly higher precision.

The mean first shell coordination number, obtained by integration of the radial distribution function $n(r) = 4\pi r^2 g(r)$ over the limits of the first peak in the $g(r)$ yield values close to 6 at elevated temperatures, and values close to 5 at the lowest temperatures investigated. An uncertainty of 0.5 is associated with the coordination numbers obtained in this study, but the relative differences in coordination are measured with a substantially greater precision.

Figure 3 compares the coordination numbers for liquid silicon as a function of temperature obtained from a number of investigators. The first point is that the present results are in excellent agreement with the earlier study reported by Ansell, *et al* [4]; the slight differences in coordination number are well within the stated uncertainties. Also included in this figure are the results of Kimura *et al* [16]. It is clear from Fig. 3 that the results of Kimura *et al* [16] differ substantially from all other measurements (including the present work) at or above the melting point and differ considerably in the trend with temperature.

In the present study, measurements were obtained at temperatures of up to 250K below the equilibrium melting temperature. The change in the coordination number with temperature and the magnitude of the coordination number near the supercooling limit are both in excellent agreement with the predictions of Angell and Borick [1-3]. The present study provides substantial support to this model which also predicts the occurrence of a first order liquid-liquid phase transition for silicon at somewhat lower temperatures (1350K) and a coordination of 4.6. Extrapolation of the present results to a coordination of 4.6 yields a transition temperature below 1300K, somewhat lower than the MD predictions. However, this is entirely consistent with the temperature at which the liquid density is expected to reach a maximum value.

A detailed analysis of the present results and a discussion of the results can be found in a full length article that has been submitted for publication. A draft copy of the article can be provided on request.

Concluding Remarks

In summary, we have presented results from a new series of x-ray diffraction experiments performed on normal and deeply supercooled liquid silicon. The new results were obtained over a wide Q-range with excellent statistics. The measured structure factor for silicon shows a well-defined primary peak at a Q of around $2.7\text{\AA}^{-1}$ and a very well-defined shoulder on the right side of this primary peak. The shoulder becomes very pronounced with increased supercooling, and becomes a very distinct feature near the supercooling limit. No abrupt changes in the structure were observed over the entire liquid range. In addition, we presented the first results on liquid SiGe alloy (equiatomic). The present results for liquid Si are in excellent agreement with the previously reported measurements of Ansell, *et al* [4], and indicate that the first shell coordination of silicon decreases continuously with increased supercooling.

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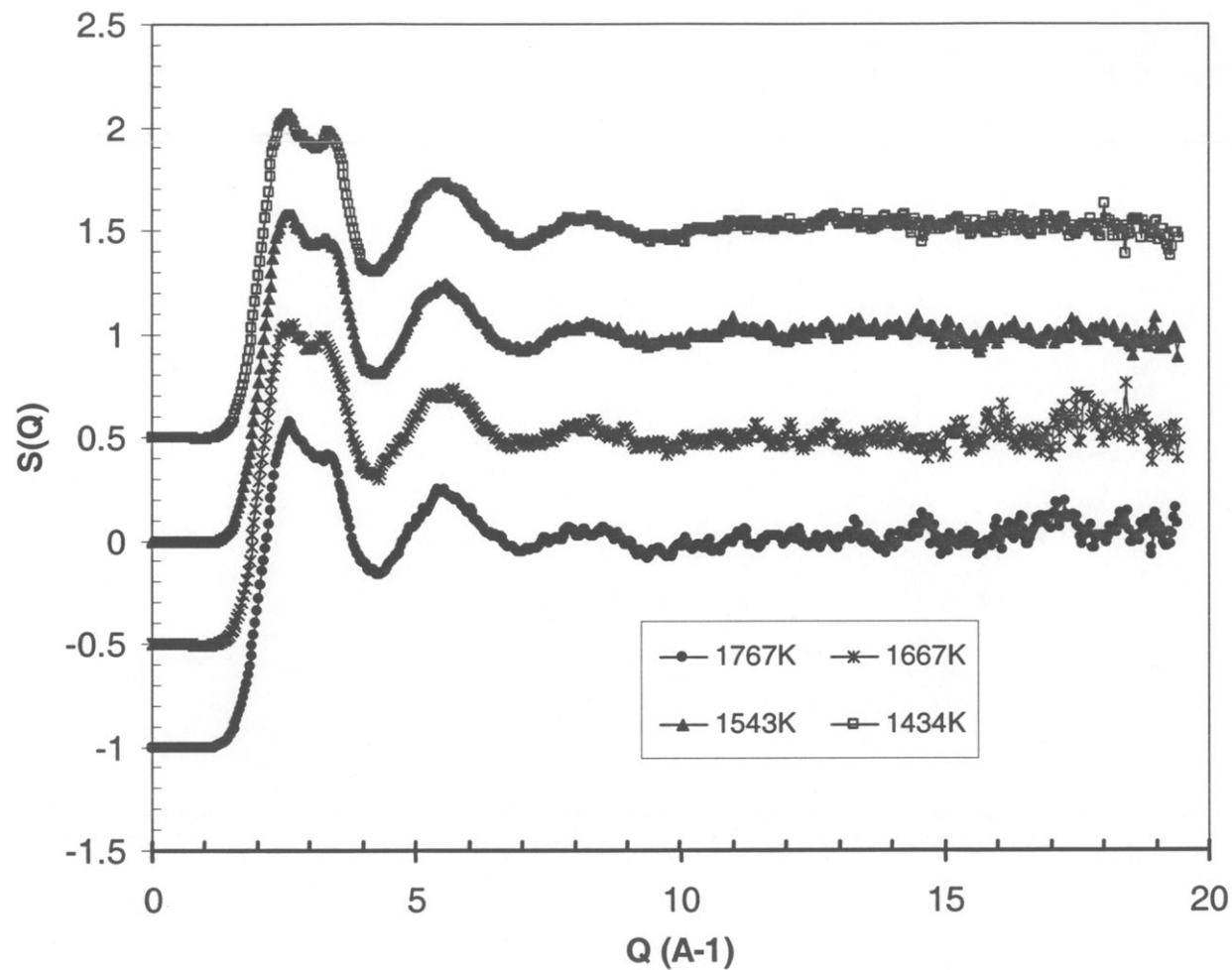


Figure 1: X-ray weighted average structure factor, $S(Q)$, for liquid Si at four temperatures (see legend), including the deeply supercooled state. Each of the curves have been displaced by 0.5 units for clarity. The bottom curve corresponds to the highest temperature while the top curve corresponds to the lowest temperature.

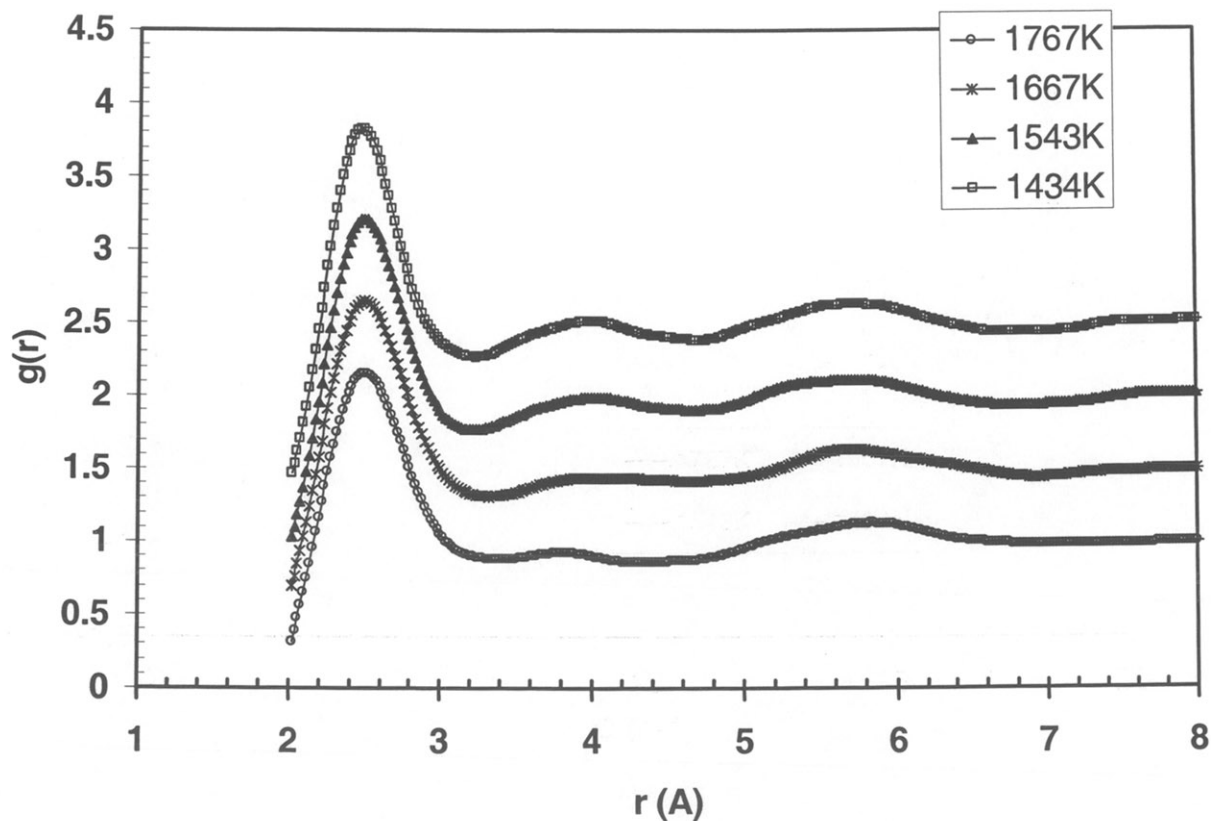


Figure 2: Pair correlation functions, $g(r)$ for liquid Si at four temperatures (see legend), including the deeply supercooled state. Each of the curves have been displaced by 0.5 units for clarity. The bottom curve corresponds to the highest temperature while the top curve corresponds to the lowest temperature.

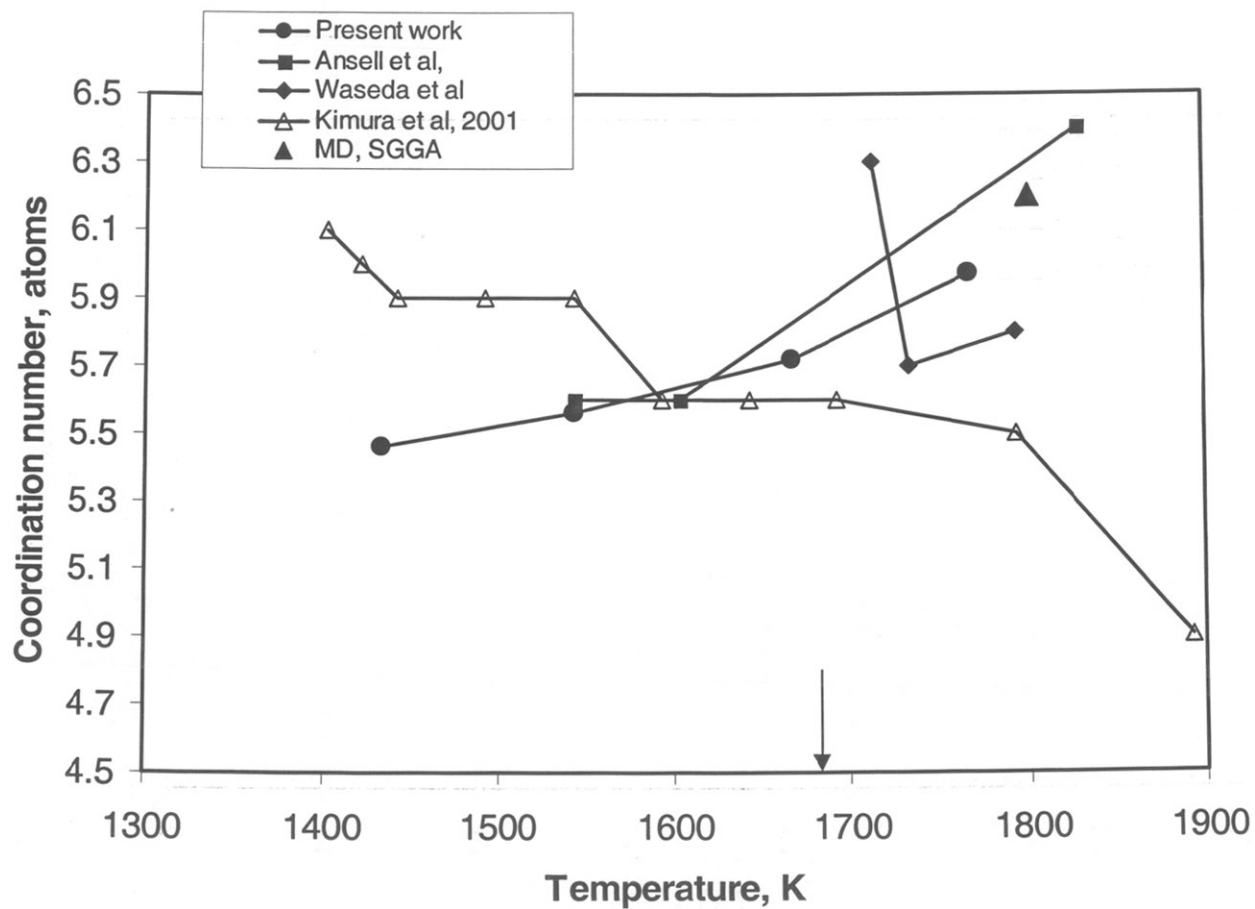


Figure 3. First shell mean coordination numbers for liquid Si obtained in the study compared to results from Ansell, *et al* [4], Kimura, *et al* [16] and other literature data. The arrow on the x-axis marks the melting point of 1688K.

DEFECT, KINETICS AND HEAT TRANSFER OF CDTE BRIDGMAN GROWTH WITHOUT WALL CONTACT

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CdZnTe is one of technologically important II-VI compound semiconductors. CdZnTe has been mainly used as a substrate material for the epitaxial growth of HgCdTe infrared detectors. CdZnTe crystal is typically grown using unseeded, horizontal or vertical Bridgman crystal growth techniques. The Bridgman growth technique has advantages of being easily instrumented and interface curvature can be readily adjusted by changing the temperatures at the top and bottom of the gradient. The disadvantage of the Bridgman growth technique is that the crystal contacts the ampoule wall, which may result in increasing the mechanical stress, impurity level, and defect density in the grown crystal. The disadvantage can, however, be overcome by the detached solidification technique (growth without wall contact).

We have proposed to grow a CdZnTe crystal without wall contact using a unique soft wall technique. The objectives of the proposed research include: (a) understanding the mechanism of detached solidification, designing the furnace, and determining the optimal growth conditions; (b) understanding the role of microgravity in detached solidification; (c) investigating the effect of detached solidification on solidification interface, stoichiometric control and macrosegregation; and (d) studying the effect of detached solidification on stress reduction, dislocation and twinning. An integrated numerical model for detached solidification has been developed combining a global heat transfer sub-model and a wall contact sub-model for the proposed modified Bridgman system. The global heat transfer sub-model accounts for heat and mass transfer in the multiphase system, convection in the melt, macro-segregation, and interface dynamics. The location and dynamics of the solidification interface are accurately tracked by a multizone adaptive grid generation scheme. The wall contact sub-model accounts for the meniscus dynamics at the three-phase boundary, which is similar to the model proposed by Duffar et al.¹ This sub-model has been used to investigate the effects of various geometric parameters, e.g., growth angle, wetting angle, number density, and shape of the finned structure on the CdZnTe detached growth. The global heat transfer sub-model has been used to investigate the effects of the carbon velvet fins on heat and mass transfer in the furnace and detached solidification, and the effects of detached solidification on stoichiometry, micro/macro-segregation under micro- and normal gravity conditions. Simulations have been performed for crystal growth in a conventional ampoule and the designed ampoule to understand the benefits of the detached solidification and its impacts on crystalline structural quality, e.g., stoichiometry, macro-segregation, and stress. The integrated model can be used in designing apparatus and determining the optimal geometry for detached growth in space and on the ground, and the effects of detached solidification on dislocation density and twinning formation will be investigated in the near future.

1. Background and Objectives

Cadmium-Zinc-Telluride (CdZnTe) crystals were grown in unit gravity and in μ -g for comparative analysis in our prior program, Orbital Processing of High Quality Doped and Alloyed CdTe Compound

Keywords: directional solidification, Bridgman crystal growth, defects, wall contact, new research

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Semiconductors. Two Zn alloyed CdTe crystals were grown on USML-1/STS-50 in 1992, and two additional crystals were grown on USML-2/STS-73 in 1995.² The Crystal Growth Furnace (CGF) in the seeded Bridgman-Stockbarger crystal growth geometry was utilized on both missions. Crystals grown on USML-1/STS-50 were found to have solidified with partial wall contact due to the near-absence of the hydrostatic pressure in μ -g, the absence of melt volume constraint, a residual g-vector that was not axial, and non-wetting sample/ampoule wetting conditions. Crystals grown on USML-2 /STS-73 were grown with a non-axial residual gravity vector, and included: a sample/ampoule identical to the USML-1/STS-73 sample/ampoule, with the addition of a restraining spring to simulate hydrostatic pressure internally; and a tapered ampoule intended to minimize wall contact. A crystal with 2.2 cm without wall contact and 2.8 cm with partial wall contact has been accomplished.

Infrared transmission of all ground and flight samples was found to be 63-66%, very close to the theoretical 66%, suggesting very good stoichiometric control. Longitudinal macrosegregation, calculated using scaling analysis, was predicted to be low. Nearly diffusion controlled growth was achieved even in unit gravity and macrosegregation data could be fit with a diffusion controlled model. Radial segregation was monitored and was found to vary with fraction solidified, particularly through the shoulder region, where the sample cross-section was varying significantly. In regions where a steady-state was established, the radial segregation was invariant, within our experimental measurement error. Ground samples exhibited a fully developed (111)[110] dislocation mosaic structure, whereas dislocations within the flight samples were discrete and no mosaic structure was evident. Dislocation etch pit density results were confirmed using etch pit microscopy, transmission synchrotron white beam and transmission monochromated beam topography. Dislocation density was quantitatively reduced from 75,000 (1-g) $\pm$ 50% to 800 (μ -g) $\pm$ 50%. The low defect density is thought to have resulted from the near absence of hydrostatic pressure, which allowed the molten boule to solidify with little or no wall contact. This minimized the stresses during solidification and transfer of hoop stresses during post-solidification processing.

In regions where solidification had occurred without wall contact the free surfaces evidenced virtually no twinning, though twins reappeared in the flight samples in regions of wall contact for the tapered USML-2 sample. Twinning was pervasive in the ground samples. These results were confirmed using optical microscopy and synchrotron x-ray white beam and monochromatic beam topography. The reason for the dramatic reduction in twins in regions without wall contact is without explanation, though they are thought to be largely surface nucleated.

Our efforts to extend the processing over larger regions of the crystal on USML-2/STS-73 was partially successful, using a tapered ampoule with the wall “falling away” from the triple junction. This increased the material solidified without wall contact. The goal of this research is to further our investigation of the influences of gravitationally-dependent phenomena (hydrostatic and buoyant) on the growth and quality of doped and alloyed CdZnTe. A modified seeded Bridgman-Stockbarger technique with a soft ampoule has been designed. We will study the influences of damping the gravitationally-dependent buoyancy convection on chemical homogeneity, with particular attention to chemical distribution in close proximity to free surfaces. This will address the issue of thermo-capillary flow at free crystal growth surfaces, and the influences of such flows on chemical redistribution and surface generation of defects. More to the point, however, the near-elimination of hydrostatic pressure will enable crystals to be grown in a novel soft ampoule geometry that would be impossible terrestrially. These experiments will allow us to test the origins and theory of twinning and the origins and distribution of dislocations (propagation,

annihilation, multiplication, and redistribution) in this important detector material.³ The objectives of the proposed research include: (a) understanding the mechanism of detached solidification, designing the furnace, and determining the optimal growth conditions; (b) understanding the role of microgravity in detached solidification; (c) investigating the effect of detached solidification on solidification interface, stoichiometric control and macrosegregation; and (d) studying the effect of detached solidification on stress reduction, dislocation and twinning.

2. Detached Growth Technique

CdZnTe is one of technologically important II-VI compound semiconductors. CdZnTe has mainly used as a substrate material for the epitaxial growth of HgCdTe infrared detectors. CdZnTe crystal is typically grown using unseeded, horizontal or vertical Bridgman crystal growth techniques. The Bridgman growth technique has advantages of being easily instrumented and interface curvature can be readily adjusted by changing the temperatures at the top and bottom of the gradient. The disadvantage of the Bridgman growth technique is that the crystal contacts the ampoule wall, which may result in increasing the mechanical stress, impurity level, and defect density in the grown crystal. The disadvantage can, however, be overcome by the detached solidification technique (growth without wall contact). The first report about detached growth was one of the results of the Skylab missions.⁴⁻⁵ In the intervening years, detached Bridgman growth has been observed in many microgravity experiments.⁴⁻⁹ Larson et al.^{2,10} provided extensive characterization of partially detached growth of CdZnTe crystals with respect to dislocation density, grain structure, infrared transmittance, and residual stress and strain. They demonstrated that the positive influence of detachment on the crystal quality. When detached solidification occurs, the structural quality of the crystal is improved (fewer dislocations, lower residual strain, and fewer grains), probably owing to the disappearance of stresses exerted by the crucible/ampoule on the crystal during the cooling of the crystal and reduction of heterogeneous nucleation sites.

Although tremendous advancements have been achieved in detached growth techniques, the mechanism is not well understood. Detached solidification is particularly prevalent among semiconductors. Growth angle is virtually zero for a metal and high for a semiconductor; it is therefore possible that growth angle plays an important role in this phenomenon. From the literature surveyed, it can conclude that the appearance of detached solidification seems related to crystal growth angle, wetting angle, crucible roughness, and gas pressure. In summary, detached growth will more likely appear in the following conditions:

- Large wetting angle between the melt and the crucible material,
- Large growth angle between the meniscus and the crystal surface, and
- Small gas pressure difference between the gap and the top of the melt.

All three factors affect the shape and dynamics of the meniscus and three phase boundary. Wilcox, Regel and co-workers⁶⁻⁸ and Duffar et al.^{1,9} have proposed different growth mechanisms. The model of Wilcox, Regel and co-workers⁶⁻⁸ was based on force balance between surface tension and gas pressure in the gap separating the charge and ampoule. The detailed growth model was developed accounting for segregation of the gas at the solidification interface, evaporation at the melt/gas surface, and bulk transport by the buoyancy-induced convection. The flux of the evaporating gas was related to gas pressure providing the necessary input for the calculation of the gas/melt meniscus shape. The results indicated that reduction of convection in the melt increases the gas content in the melt at the growth front leading to a more stable detached growth condition. Duffar et al.^{1,9} proposed that the surface roughness and growth angle of the ampoule were the primary reasons for detached solidification, and conducted numerical simulations aimed

at identification of the required surface roughness to achieve detached growth. Simulations focused on the kinematics of force balance at the ridges connecting the melt to the rough crucible.

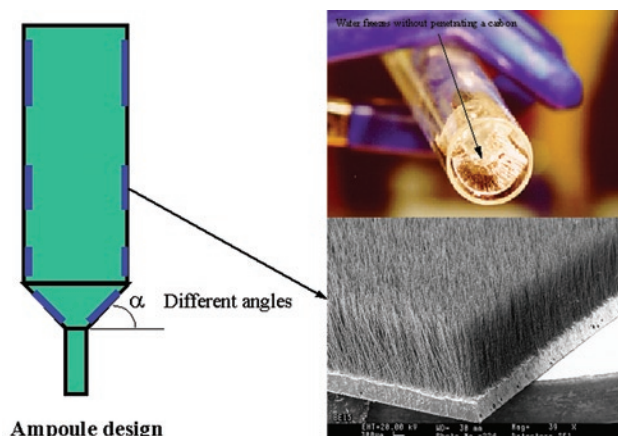


Figure 1. A novel Bridgman detached growth system using carbon non-wetting velvet.

We propose to use a cylindrical ampoule with an internal ‘multiple fin’ structure that will support the liquid in microgravity with minimum or no wall contact. A typical carbon fiber ‘velvet’ structure of this type is shown as Fig. 1. The diameter (strength and rigidity), number density, fiber end shape and wetting angle relative to CdZnTe, and velvet material can be engineered. It has been made into ampoule configurations. CdZnTe does not wet Carbon, so it should resist penetrating the velvet. Also shown in Fig. 1 is that a low density, non-wetting fluid (H_2O), that expands on solidification, can be solidified without penetrating the fibers. This is what we propose to do in microgravity with CdTe. We will use the multifin annular regions for active atmosphere stoichiometric control, and fluid/crystal support. The advantages of the proposed design include stoichiometric control and meniscus control, since the vapor can be transported freely between the fins and contacts the melt fully.

In this proposal, we will develop a numerical model which can be used to understand the difference between crystal growth in a smooth ampoule and in a soft-wall ampoule and determine the optimal fin structure for the maximum possibility of detached growth of CdZnTe. A length of crystal will be grown and then the velvet will be discontinued for a length less than the Rayleigh instability length, at which point the velvet will be reintroduced. Schematic of such ampoule is shown in Fig. 1. This is case I, where the twin density will be tested with and without contact, with a constant geometry. Two runs are proposed. The first will be solidified with a concave interface, which should deter facet formation and twinning. The second will be run with a convex interface, which should promote facet formation and twinning. Our second experiment series, Case II, will employ the same ampoule type, except with connected sections with different inner diameters. The connecting fluid sections will reproduce the shouldering region of a Czochralski geometry. Fluid statics will determine the meniscus shape, which will be predicted by our model. An increasing diameter and a decreasing diameter will be investigated with concave and convex interface shapes, as in Case I. This will offer unique insight into the twinning problem.

3. Integrated Model in Bridgman Growth System

In order to improve the electronic properties of semiconductor crystals produced from a liquid phase, it is essential to reduce the number of defects caused by convection-induced movement within the liquid, such as growth oscillation or longitudinal or radial differences in chemical composition. Crystal growth

experiments performed in microgravity have shown that, as forecast by theoretical considerations, homogeneous solutal distribution profiles can be obtained nearly without convection.^{4-5,11} Detached solidification in microgravity results in a crystal surface state without any apparent relation to the surface state of the crucible/ampoule. When detached solidification occurs, the structural quality of the crystals is improved. Its appearance seems related to numerous factors: crystal growth angle, wetting angle, and crucible roughness.

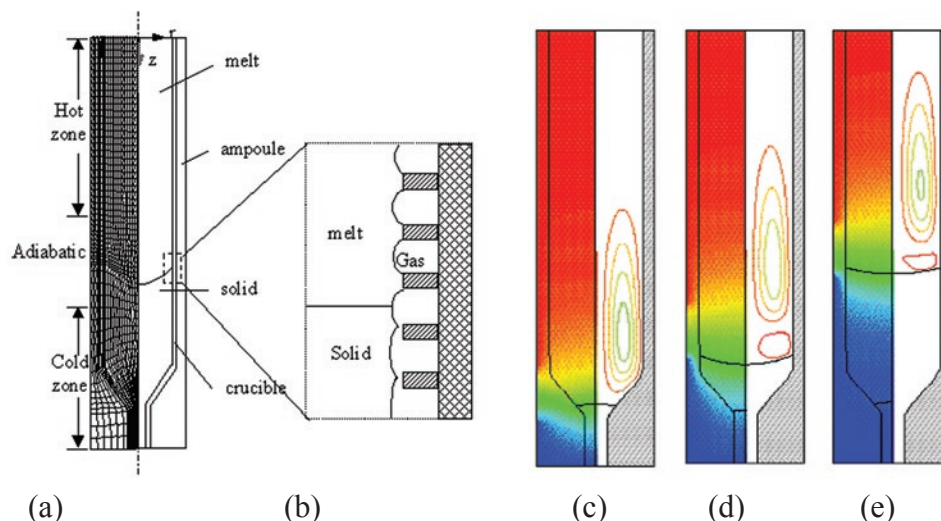


Figure 2. (a) Schematic of a modified Bridgman growth system. (b) an enlarged view at the three-phase boundary. (c-e) Simulation results for the designed experiment.

Major progress has been made in the simulation of Bridgman and other crystal growth from the melt techniques. The current research focuses on high resolution three-dimensional transient simulation, convective heat and mass transfer, gravitational and thermal stress, interface morphology and dynamics, free surface deformation, interaction between the ampoule and crystal, correlation between the defect and stress, micro- and macro-segregation and so on. Major progress has been made in the simulation of Bridgman growth of CdTe and CdZnTe crystals¹². To simulate detached growth in a Bridgman system, Popov et al.⁷ have assumed that a gap forms between the solid and the ampoule wall and a meniscus forms between the wall and the edge of the freezing interface. According to their paper, the dissolved gas is transported into the gap across the meniscus, affecting the pressure in the gap and the gap width. A numerical model was developed to account for heat transfer in the multiphase system (solid, liquid and gas), convection in the melt, and transport of dissolved gas. The locations of the solidification interface and meniscus are tracked explicitly. The stability and heat transfer were investigated.

A state-of-the-art computer model, *MASTRAPP* (Multizone Adaptive Scheme for TRANsport and Phase-change Processes) will be used for the numerical simulation. The model solves governing equations of mass, momentum, energy and chemical species to predict the flow and heat transfer in a system¹³⁻¹⁶. The numerical scheme is capable of capturing the interface shape and location efficiently and accurately since the interface velocity and shape are directly related to interface instability, and defect generation. The model has been extensively used for modeling and simulation of crystal growth. The *MASTRAPP* can account for global heat and mass transfer in a crystal growth system. The computer code can also predict the thermo-elastic stress in as-grown crystals based on the temperature field history. It can help in correlating the defect generation in the crystal to growth conditions. Transient solute or impurity

transport in the melt is also incorporated in the model to predict the macro-segregation of dopants and alloying elements. For the proposed system, the solid/melt interface and meniscus were tracked explicitly using the multizone adaptive grid generation scheme. The finned wall were modeled by straight fins of uniform or non-uniform cross section. The heat transfer of the fins was solved analytically for a single fin or modeled for interaction between the fins. The analytical and numerical results were integrated into the global/dynamical model. Figures 2(a-b) show the schematic diagram of the designed Bridgman system, and Figs. 2(c-e) show the shape of solidification interface and temperature distribution in this system. In this simulation, the soft wall is modeled as a solid layer attached to the crucible with different thermal conductivity, which depends on the number density of the finned structure.

Duffar et al.¹ have proposed a mechanism to explain detached solidification on a rough ampoule in space. A similar mechanism is developed for the current soft wall ampoule. A planar-front solidification of the melt in contact with the roughness tip of the crucible is assumed at $t = 0$. The hydrostatic pressure within the melt due to the gravity is assumed to be negligible, so that the melt-gas interface has a large radius of curvature, e.g., the melt-gas interface is flat. Detached growth mechanism is proposed as follows: at time $t = \Delta t$, the growth began and the interface moved a distance of $\Delta x = \Delta t \times U$, where U is the growth rate. The angle between the solidifying direction and the melt-gas interface adhering to the second roughness tip is equal to the growth angle α_g (Fig. 3a). This planar-front solidification continues in this way until the angle between the melt-gas interface and the second roughness tip reaches the wetting angle (contact angle) θ_w (Fig. 3b). At this point, the melt detaches from the roughness and the planar-front solidification repeats the same procedure until the melt attached to the next roughness tip (Fig. 3c).

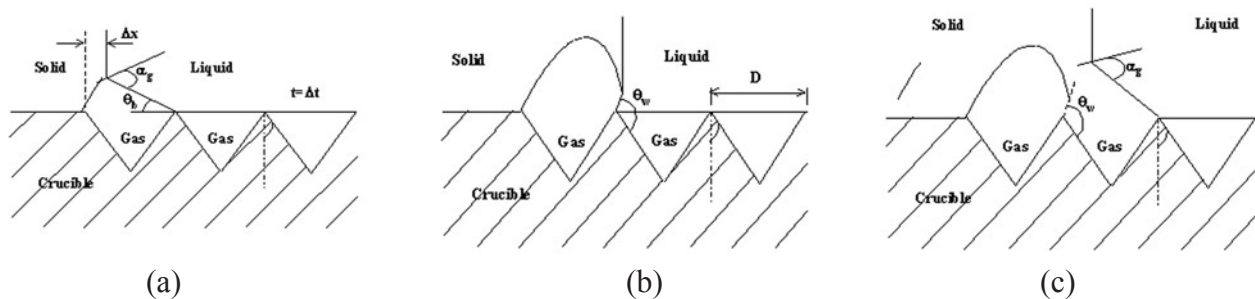


Figure 3. Detached solidification mechanism for a Bridgman crystal growth using a rough ampoule.

Based on above mechanism, Figure 4(a) shows the numerical results of detached solidification for various growth angles. Steady-state solution can be reached after about 15 fins, and only steady-state portion of the solution has been shown in Fig. 4(a). It can be seen that detached gap width changes dramatically as the growth angle changes. From numerical results, it is clear that detached thickness is dependent on growth angle, wetting angle, and gap width and shape of the fins. It is proved that a large wetting angle and a large growth angle do promote detached growth. We can also conclude that a large gap width, D , may also be benefit for detached growth in space experiment. Other interesting conclusions include, if the growth angle α_g is too small, for example, less than 10° , the detached growth will not happen. Since the growth angle of CdZnTe cannot be changed, to promote detached growth, the number density of the fins should be low and the wetting angle should be high. The shape of the fins has minor influence on detached growth.

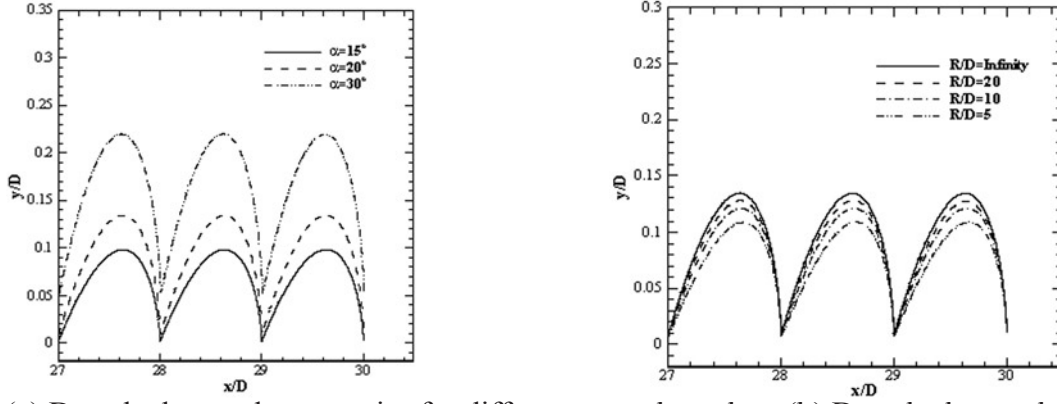


Figure 4. (a) Detached crystal geometries for different growth angles. (b) Detached crystal geometries for different liquid-gas interface curvature.

For detached growth on the ground, the effect of gravity has to be considered. The melt-gas interface will not be flat. We will introduce a new parameter, the melt-gas interface curvature, $R = \frac{\sigma}{\rho_L g h}$ where σ is the surface tension (kg/s^2), ρ_L is the density of melt (kg/m^3), g is the gravity acceleration (m/s^2), h is the height of melt (m). When the following parameters $\sigma = 0.72$, $\rho_L = 5680$, $g = 9.81$, $h = 0.1$, are chosen, $R = 1.29 \times 10^{-4} \text{ m}$ is calculated. It means that the gap width of the fins should be much smaller than $129 \mu\text{m}$ in the ground experiment. Otherwise, the melt will penetrate in the fins and attach the crucible. Figure 4(b) shows the effect of R/D on detached growth, in which the roughness gap D increases from $7 \mu\text{m}$ to $26 \mu\text{m}$. Noted that a much smaller D value is used here, since a much smaller D value should be used in the ground experiment. The detached gap width decreases as gravity influence increases¹⁴⁻¹⁶.

4. Gravity Effects

A sessile drop is used to study the roles of wetting angle (contact angle) and finned structure on detached growth. Since surface tension of a CdZnTe melt is not available, the surface tension of silicon, 720 dyne/cm , has been selected. The surface tension of most semiconductors is about 10 times larger than that of water. Based on this value, the Bond number, $Bo = 0.033$, corresponds to a spacing of 1 mm between fins. The shapes of sessile drop at different melt volumes are shown in Fig. 5. In the designed ampoule, the spacing between the fins is much smaller than 1 mm . Spherical shape of meniscus can therefore be assumed in the ground experiment since the Bond number is much smaller than 0.033 . The assumption used to obtain Fig. 4(b) is therefore reasonable. Equilibrium contact angles of 180 degrees means that the melt is total dewetted from the ampoule. In this case, a drop may cover several fins.

5. Heat Transfer in the Designed System

The geometric configuration of the modified Bridgman system is shown in Fig. 2. The molten CdZnTe is contained in a cylindrical ampoule with soft-finned wall. During a typical seeded Bridgman-Stockbarger growth of CdZnTe, crystal growth is accomplished by establishing isothermal hot zone (1175°C) and cold zone (980°C) temperatures with a uniform thermal gradient (35°C/cm) in between. Having seeded the melt, the sample is thermally equilibrated and the sample is directionally solidified at a constant velocity (1.6 mm/hr) by moving the furnace and thermal gradient down the length of the stationary sample, ampoule, and safety cartridge. During detached growth, a gap is formed between the as-grown crystal and the ampoule wall and a meniscus is formed between the edge of the freezing interface and the fin. The vapor can be transported freely into the gap through the multiple fins. CdZnTe crystal exists

as a semiconductor in the liquid phase, and molten CdZnTe exhibits very low thermal conductivity. This feature, coupled with rather high viscosity, leads to the molten state of the material being characterized by a moderate Prandtl number of $Pr = 0.406$, a value that is roughly thirty times larger than that of most semiconductors, such as Si, GaAs, and InP. A value of order one implies a strong two-way coupling between thermal and momentum transport, which distinguishes the behavior of Bridgman CdZnTe growth from growth of other semiconductors.

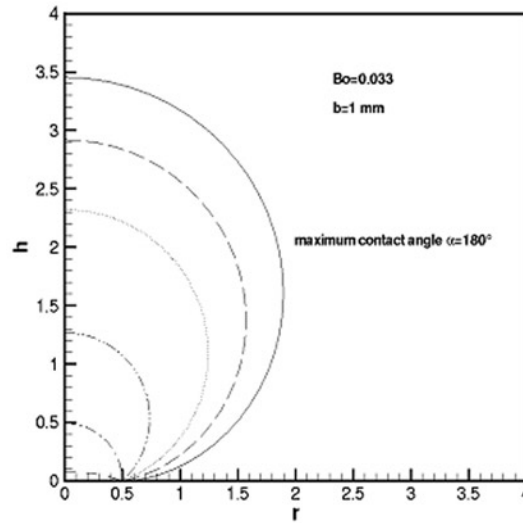


Figure 5. Effect of gas volume on the shape of the sessile drop for the Bond number of 0.033.

To grow a 5.0 cm diameter CdZnTe crystal, the Grashof number $Gr = 1 \times 10^5$ is equivalent to temperature at the hot zone $T_h = T_f + 21.43$ using the physical properties of CdZnTe^{12,15}. Noted that $T_h = T_f + 83$ is used in the USML-2 experiment. It is safe to say that the Grashof number will vary from 5×10^4 to 10^6 for the designed system. A set of baseline parameters, $Pr = 0.406$, $Gr = 1 \times 10^5$, $Ste_s/Ste_t = 1$, and thermal conductivity of the finned structure, $K_f = 8.5$, are selected to investigate the sensitivity of the fin structure on detached solidification. Parametric study was performed to examine the effects of governing parameters, e.g., the Grashof and Prandtl numbers, thermal conductivity of the multiple fin structure, and the position of the solidification interface on detached growth.¹⁵⁻¹⁶ Numerical simulations have been performed for the upper and lower bounds of the parameter. Results show that convection is very strong for the Grashof number of 10^6 . The fluid and temperature patterns are somewhat similar to those in a tall cavity or cylinder for the Pr number of unity. The flow field is weaker and the interface is less curved if the Grashof number is reduced. It can be concluded from numerical simulations that the interface shape is mainly determined by the melt convection in the designed system. This conclusion is different from the Bridgman growth of other semiconductor materials with low Prandtl number. Convection effects are much more significant in the growth of CdZnTe due to the strong coupling between fluid flow and temperature distribution. The crystal growth will therefore be very different in space and on the ground.

The effects of thermal conductivity of a fin structure on fluid flow, temperature distribution and interface shape are presented in Figs. 6(a), 6(b) and 6(c) for three different values of thermal conductivity of the fin structure, $K_f = 0.907$, 8.5, and 85, respectively. The fluid flow is weaker if thermal conductivity of the fin structure is lower. However, the effect of thermal conductivity of the fin structure on the interface shape is not significant. This conclusion is not surprising since conductivity of CdZnTe crystal is very low. The

effect will be much significant if thermal conductivity of the growing crystal is higher. More parameter studies have been performed, which can be found in the published papers.¹⁵⁻¹⁶

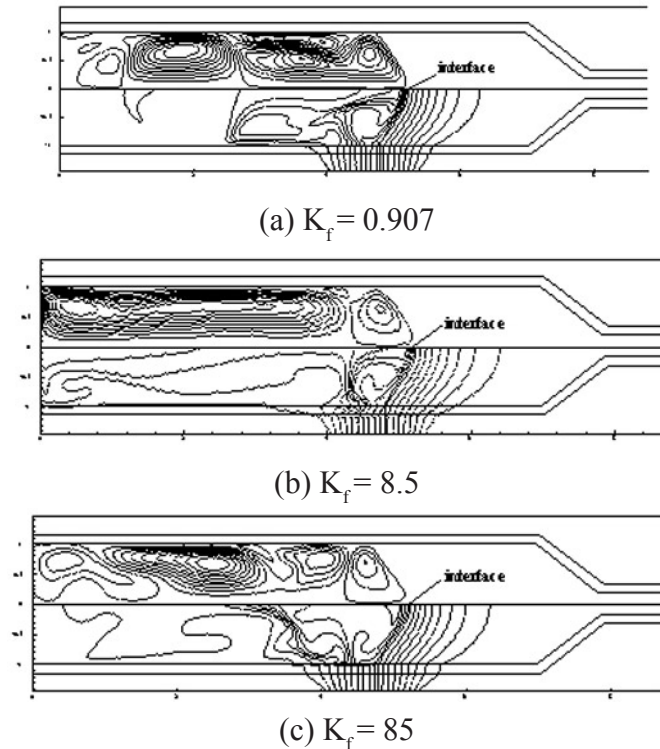


Figure 6. Effects of thermal conductivity of the fin structure on fluid flow, temperature field, and interface shape in a modified Bridgman growth system with $Pr=0.406$, $Gr=1.0e6$, $Ste_s/Ste_t = 1$, $K_s = 9.07 \times 10^{-1}$, $K_l=1.085$, $K_a=85$.

6. Zn Concentration Distribution In the Designed Furnace

The effects of the Grashof number on Zn concentration distribution in the CdTe melt are investigated. The change of melting temperature with composition is considered though phase-diagram^{15,16}. Numerical results are presented in Fig. 7. The concentration boundary layer thickness at the center of the melt increases when the Grashof number increases from zero to 10^3 , and decreases shapely when the Grashof number increases from 10^3 to 10^4 . Space experiments showed that nearly diffusion controlled growth were achieved and the radial segregation was found to vary with fraction solidified, particularly through the shoulder region, where the sample cross-section was varying significantly. In regions where a steady-state was established, the radial segregation was invariant. Numerical results show that the radial segregation will also vary significantly when the solidification interface passes through the shoulder region, where the Grashof number changes rapidly, in the ground experiment.

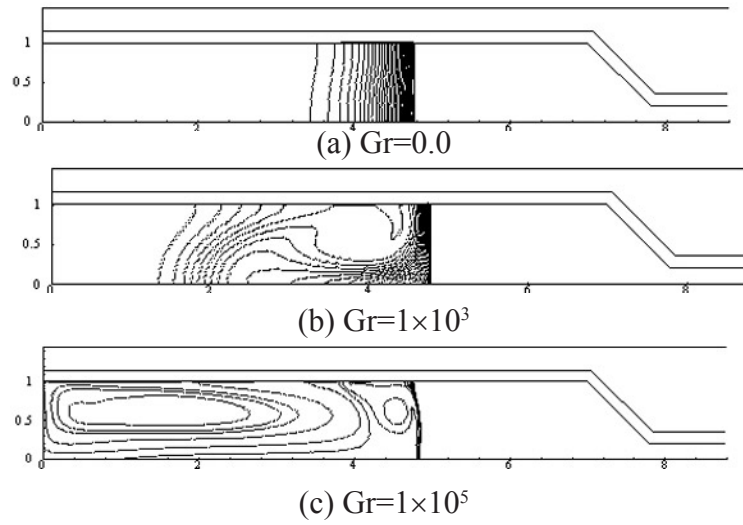


Figure 7. Concentration distributions in the ampoule for $Sc = 41.5$, $k = 1.35$, and (a) $Gr=0$, (b) $Gr=10^3$, and (c) $Gr=10^5$ in a modified Bridgman growth system.

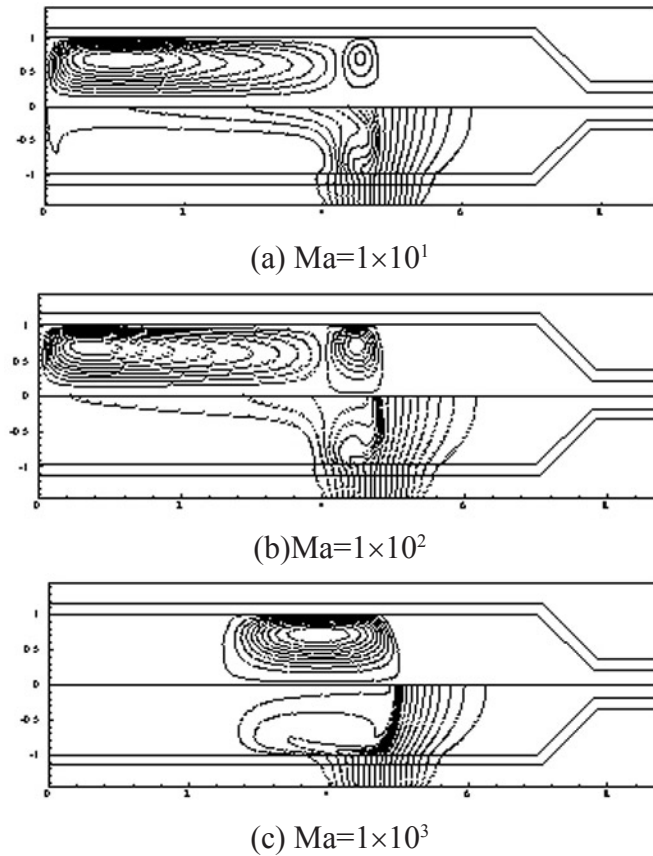


Figure 8. Effects of the Marangoni number on fluid flow and temperature distribution for $Gr=1 \times 10^5$.

7. Marangoni Convection during Detached Growth

Duffar et al.^{1,9} and Levenstam et al.¹⁷ have pointed out that Marangoni convection will be important in fully or partially detached growth. To model the partially detached free surface, Levenstam et al.¹⁷ have

derived a tangential velocity boundary condition, which is a function of the fraction of free surface and the temperature gradient over detached region. Assuming that two-dimensional assumption is still valid and the equivalent Marangoni number can be used, the effects of Marangoni convection on the interface shape and temperature distribution are illustrated in Fig. 8. In this calculation, the Marangoni number is determined by the size of the ampoule and temperature difference between the hot and cold zones. As the Marangoni number increases, temperature gradient in the melt near the interface increases. It makes the solidification interface move to the cold side. The shape of solidification interface has also varied. Furthermore, the cell above the interface becomes much stronger as the Marangoni number increases. Consequently, Zn concentration distribution and radial segregation will vary significantly.

8. Conclusions

A detached growth mechanism has been proposed, which is similar to that proposed by Duffar et al.¹ and used to study the current detached growth system. From numerical results, we can conclude that detached growth will more likely appear if the growth and wetting angles are large and meniscus is flat. Detached thickness is dependent on growth angle, wetting angle, and gap width and shape of the fins. The model can also explain why the detached growth will not happen for metals in which the growth angle is almost zero. Since the growth angle of CdZnTe cannot be changed, to promote detached growth, the number density of the fins should be low and the wetting angle should be high. Also, a much smaller gap width of the fins should be used in the ground experiment and the detached gap width is much smaller. The shape of the fins has minor influence on detached growth. An integrated numerical model for detached solidification has been developed combining a global heat transfer sub-model and a wall contact sub-model. The global heat transfer sub-model accounts for heat and mass transfer in the multiphase system, convection in the melt, macro-segregation, and interface dynamics. The location and dynamics of the solidification interface are accurately tracked by a multizone adaptive grid generation scheme. The wall contact sub-model accounts for the meniscus dynamics at the three-phase boundary. Simulations have been performed for crystal growth in a conventional ampoule and a designed ampoule to understand the benefits of detached solidification and its impacts on crystalline structural quality, e.g., stoichiometry, macro-segregation, and stress. From simulation results, both the Grashof and Marangoni numbers will have significant effects on the shape of growth front, Zn concentration distribution, and radial segregation. The integrated model can be used in designing apparatus and determining the optimal geometry for detached solidification in space and on the ground.

9. Acknowledgements

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NANOPARTICLE ENGINEERING OF COMPLEX FLUID BEHAVIOR

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A new mechanism for regulating the stability of colloidal particles has been discovered. Negligibly charged colloidal microspheres, which flocculate when suspended alone in aqueous solution, undergo a remarkable stabilizing transition upon the addition of critical volume fraction of highly charged nanoparticle species. Zeta potential analysis revealed that these microspheres exhibited an effective charge buildup in the presence of such species. Scanning angle reflectometry measurements indicated these nanoparticle species did not adsorb on the microspheres under the experimental conditions of interest. It is therefore proposed that highly charged nanoparticles segregate to regions near negligibly charged microspheres due to their repulsive Coulombic interactions in solution. This type of nanoparticle haloing provides a new method for tailoring the behavior of complex fluids, including its flow properties and structure.

Keywords: new research

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MAGNETIC FIELD EFFECTS ON CONVECTION AND SOLIDIFICATION IN NORMAL AND MICROGRAVITY

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Abstract

It has been well understood that convective flows induced by g-jitter forces associated with spacecraft are responsible for defects formation and irregularity in product quality during melt growth of single crystals in microgravity. This research is concerned about numerical simulations and experimental measurements for the purpose of developing a fundamental understanding of the g-jitter induced fluid flows and their effects on solidification in microgravity with and without the presence of additional damping forces that are derived from the applied DC magnetic fields. The numerical models include both 2-D and 3-D transient fluid flow, heat transfer, mass transfer and solidification under the combined action of g-jitter and magnetic fields. Numerical simulations using both the 2-D and 3-D models are conducted for both idealized, synthesized and real g-jitter forces, and 2-D simulations are tested against the experimental measurements taken on the thermal oscillator. 2-D solidification models have also been developed and simulations are conducted. Results show that the numerical model predictions compare well with the measurements. Analysis of these results illustrates that an applied magnetic field can have a drastic influence on the convective flows induced by g-jitter and can be particularly useful to suppress the effects resulting from the spiking of g-jitter signatures, which are considered the most detrimental effects on quality of crystals grown in space. Work in progress includes developing 3-D numerical models for solidification phenomena with the presence of both g-jitter and magnetic fields and measurements of flow fluid and its effect on solidification in both transparent fluid and low melting point melts to verify numerical predictions.

I. Introduction

Microgravity and magnetic damping are two mechanisms applied during the melt growth of semiconductor or metal crystals to suppress buoyancy driven flow so as to improve macro and micro homogeneity of the crystals. As natural convection arises from gravity effects, microgravity offers a plausible solution to reduce the convective flow. However, recent flight experiments indicate that residual accelerations during space processing, or g-jitter, can cause considerable convection in the liquid pool, making it difficult to realize a diffusion controlled growth, as originally intended, when experiments were conducted in microgravity [1]. Further studies showed that g-jitter is a random phenomenon associated with microgravity environment and has both steady state and transient effects on convective flow. Since molten metals and semiconductor melts are electrically conducting, magnetic damping may be explored to suppress the unwanted g-jitter induced convection during solidification [2].

The objective of this work is to further develop and verify numerical capabilities in support of microgravity materials science programs involving the use of magnetic fields to dampen convection. The objectives

Keywords: magnetic damping, g-jitter induced convection, solidification, electromagnetic levitation, electrostatic levitation

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of the proposed research are to (1) conduct measurements of oscillating melt flows in physical models, and to verify and refine the melt flow model developed for g-jitter induced flows against the measured data; (2) assess the effect of oscillating convective flows on solidification in a microgravity environment through numerical modeling and ground-based laboratory measurements; and (3) understand and quantify the effect of convective flow enhancement in a DC magnetic field, whose main action has so far been understood to provide damping effects on convection. Significant progress has been made in achieving the objective and research results are presented in several publications [3-17]. Below we discuss some crucial results, some of which are still being further analyzed.

II. Experimental Measurements

A physical model using transparent fluids such as water and SCN has been established to study the oscillating flow induced by oscillating thermal gradient and the effect of fluid flow on solidification. The detailed experimental setup is shown in Figure 1. The system consists of three computers, a laser generator, a CCD camera, a test cavity cell, a heat stripe, two isothermal water baths and an expansion board. The function of the computer on the left is to collect temperature data and to control the shutter of the CCD camera for flow visualization and PIV measurements. Two integrated circuit boards (CIO-DAS 1402/16 and CIO-CRT05, both from ComputerBoards Inc.) were installed in the computer, with the former for analog/digital conversion, and the later the control of shutter speed of the CCD camera. The middle computer is to control the heat stripe mounted on the test cell. It uses its own counter board and sends signals to the AC power generator (Model XHR 150-7 from XANTREX Com.) to generate the oscillating electrical wave required to produce an oscillating temperature field. The computer on the right is a dual processor PC, designed for data intensive computations for image processing. It combines image capturing and image processing into one unit. Its high speed and big memory makes it possible to save the images as fast as needed for our applications. This computer is synchronized with that on the left to obtain the temperature and velocity at the same time.

The main part of the system is a rectangular cavity with a dimension of $1.80\text{cm} \times 2.03\text{cm} \times 15.0\text{cm}$. The length is 6 times more than the height and width to eliminate the 3-D effect. The top and bottom walls were made of 1.27cm thick acrylic. Also some polystyrene was glued on these plates for insulation purpose. The two side walls were made of 3.16mm thick grade copper in order to get good heat conduction. To prevent the copper side walls from reflecting laser's light, black layer was painted on the inside surface of the side walls.

Before any measurements were taken, the water was allowed to flow through the thermobaths (or thermomixers) for about half an hour to establish a steady state. Then the required frequency was turned on and the heater was activated, while the temperature along two side walls was monitored. Various testing cases showed that after 5~6 cycles, the temperature and the fluid flow reached a quasi-steady harmonic motion. In our case, the lowest frequency used was about 0.01Hz. That means both the flow and temperature become quasi-steady within 10 minutes, or 6 cycles. To ensure the fully oscillated condition so as to collect data for comparison with the numerical modeling, it was allowed to run more than 30 minutes before starting to collect temperature data and capture the images.

III. Comparison of Simulations with Experiments

We have developed both 2-D and 3-D numerical models for the transient fluid flow, heat transfer and solutal transport under the influence of g-jitter with and without the presence of an external magnetic

field. The model development was based on the finite element solution of the transport equations with the Lorentz forces as a momentum source and entails the modification of our in-house finite element fluid flow and heat transfer code. The numerical models were further tested against the analytical solution for the application of magnetic damping to suppress the g-jitter induced convective flows, and excellent agreement exists between the two approaches [4,5]. With the numerical models, extensive simulations have been carried out [6-16].

Experiments were conducted for various configurations and different conditions. As noted in previous studies, for space applications the low frequency has the most important effect. Numerical simulations of g-jitter driven convection show that the most detrimental effects come from the frequency range of 0.01 to 0.5 Hz, which is the approximate range of studies. To produce an oscillating thermal gradient, the temperature at one wall is fixed and that at the opposite is oscillated, with the mean temperature being the fixed wall temperature. This implementation gave a very stable wall temperature oscillation after a short transient period.

Figure 2 shows the oscillation of convection patterns, along with the computed results for the oscillation frequency of 0.025 Hz. As the flow is transient and evolves in time, only some of the snap shot pictures can be presented here. These snap shots of the transient convection reveal some of the very essential features of the convection in the system. Examination of these figures illustrates that both the experimental measurements and the numerical simulations are in excellent agreement. Both the measured and computed results show that the liquid convection in the cell responds to the temperature changes in time. A large convection cell is developed initially, circulating down along the cold wall and moving upward along the hot wall, as shown in Figure 2a1 – a3. The icon of this large flow cell is located closer to the hot wall as well to satisfy the mass conservation across the liquid pool. It is noticed that the flow near the hot shows a high velocity magnitude and it becomes weak near the cold at the instant. Near the lower corner of the cold wall, a smaller, weak and anti-rotating flow eddy develops and appears to contribute to the weakening of the convection along the cold wall.

The convective flow field continues to evolve in response to the temperature change in time. The weaker and smaller cell appearing at the low corner of the liquid pool, as shown in Figure 2a3, continues to grow in strength and invade in to the territory of the large cell. As the temperature decreases at the hot wall below the cold temperature, the initially small cell takes the entire liquid pool, reversing the global flow structure completely. This is clearly seen in Figures 2c3, where the temperature at the hot wall is actually reduced below the cold wall temperature, thereby causing the flow reversing. There appears to be a rather weaker and small flow cell developing at the upper corner near the cold wall. The comparison of measured and calculated velocities at two specific locations, as evolving in time, is illustrated in Figure 3. Evidently, there exists gratifying agreement between the experimental measurements and numerical model predictions. Analyses of the measured and computed results show that there exists a phase angle between the temperature variation and the flow oscillation and this phase angle depends on many factors. The angle is a function of location, the applied temperature and the oscillating frequency, which confirms our early studies [4-7].

Early analyses have suggested that the perturbations of high frequencies produce small or negligible effects on convection and solutal striation but offered no physical explanation. That the high frequency component does not affect the flow motion is confirmed by our experimental measurements and

corresponding numerical simulations, as shown in Figure 4, for an oscillating frequency of 0.1 Hz and beyond. Here it is apparent that the convection in the liquid is no longer oscillating, despite the oscillating temperature gradients applied on the two opposite walls. For this case, both the experimental measurements and numerical simulations depict two anti-rotating, steady state flow cells, equal in size and strength, which are recirculating in the entire liquid pool. To explore the reasons how the frequency truly affects the convection, a set of numerical simulations, using the finite element model verified through the experimental measurements described above. These simulated results show that, while temperature is forced to oscillate at the hot wall to establish a oscillating temperature gradient cross the liquid pool, the oscillating is largely confined in a very thin layer of the wall, when the oscillating frequency is set at 0.1 Hz. For this case, the temperatures at both the hot and cold walls are seen to be higher than that at the center portion of the liquid pool, while still maintaining the overall heat balance.

From the experimental measurements and computed results for other conditions, it is found that the convection pattern and flow oscillation is a strong function of applied frequency and is also dependent upon the orientation of the liquid cell with respect to gravity. The orientation effects are shown in a set of snap shots of the measured and computed results at various instants for a 45° tilted configuration, where gravity points downwards (see Figure 5). Clearly, the measured and computed results for this configuration are once again in excellent agreement for both flow patterns and velocity magnitudes. The oscillating flow structures are very similar to those presented above when gravity is perpendicular to the temperature gradient, in response to the time evolution of the thermal environment. However, both the measured and computed results show some subtle and yet important differences between the two configurations, as contrasted in Figure 5cs and Figure 2bs or Figure 5ds and Figure 2cs. In Figure 5cs, the flow field is characterized by three flow cells, with two large ones, approximately equal in size and strength, occupying the entire liquid pool and a small one appearing at the upper corner of the hot wall. In contrast, for the same temperature gradient, there are only two cells, with the large one taking the majority portion of the liquid pool and the smaller barely noticed at the upper corner of the cold wall. The maximum velocities are also different for two cases.

IV. 2-D Solidification Model and Numerical Simulations

Solidification models for 2-D geometries have also been developed. Both fixed grid and moving methods have been applied to develop the models and the results obtained using both methods are the same as they should. With the above experimental system, measurements were made to determine the fluid flow field and its effect on solidification morphologies. The experiments were conducted using the SCN fluid, which has been frequently used in microgravity research community. These measured results are compared with numerical predictions. Two of these comparisons are given in Figure 6 for the cavity tilted at an angle of 45° with gravity field. To ensure consistent comparison with experimental measurements, the numerical results are obtained using the fixed grid method. Apparently, the model predictions and experimental measurements are in good agreement.

With the 2-D model developed and verified as described above, numerical simulations were further carried out to study the convection induced by g-jitter and its effect on solidification for a system being considered for space flights.

Under an idealized microgravity condition, the gravity level is $10^{-6}g_0$. This condition may be obtained when the space vehicle follows the orbit perfectly without disturbances. Numerical simulations were

carried out for this condition without an imposed magnetic field. The calculations will serve a dual purpose. The results are useful in helping to gain physical insight into the steady state behavior of the system. They also provide the initial condition for the dynamic behavior of the system when g-jitter effects set in. To consider the worst scenario, the gravity is assumed to be oriented perpendicular to the growth direction, which represents the worst scenario case. The computed results show that the flow field is dominated overwhelmingly by the growth velocity, and the thermal and solutal gradient induced convective flow recirculation is small. These results are consistent with those obtained earlier from a simplified melt flow system where solidification was not considered, confirming that these simplified models indeed provide a good approximation to the melt flows under more realistic growth conditions, as they are intended to. Temperature distributions in the growth system are largely controlled by thermal conduction, which is a direct result of small Prandtl number for the system being studied. The solute distribution, on the other hand, appears to experience a slight distortion, which results from the small convection induced by the microgravity force.

Detailed analysis shows that for this case, the solute distribution has a striation of about 7%, measured by $(C_{\max} - C_{\min})/C_{\text{average}}$ along the solid-liquid interface. This concentration non-uniformity will affect the melting temperature and thus the system performance. Figure 7 compares the computed results of concentration and the normalized melting temperature distributions along the solid-liquid interface, and the solidification interface position for the system with and without taking into account the concentration effect on the melting temperature. It transpires that with the concentration effects considered, the melting temperature is no longer a constant, which results in a noticeable change in the solidification interface position. It is thus important to include the concentration effect on the melting temperature.

Numerical simulations have been carried out to study the effect of both idealized single frequency g-jitter and real g-jitter on fluid flow and solidification with and without the presence of an applied magnetic field. In a real space environment, g-jitter perturbations are random in direction, orientation and magnitude. While the studies on the single frequency effects are of great value in helping to understand the fundamentals governing the thermally induced oscillating flows, information on the fluid flow and mass transfer in a real g-jitter environment is of both fundamental and practical significance. Numerical simulations were made using the real g-jitter data, taken from the accelerometers aboard on Space Shuttle during a typical space flight. To assess the magnetic effects, calculations were made with and without the presence of an applied magnetic field. The computed results included the evolution of the flow velocity components, the interface shapes and the concentration striation along the interface and some of these calculated results are given in Figures 8 and 9. These results show that in the absence of an applied magnetic field, the velocities experience sharp spikes, in response to the change of g-jitter forces. These spiking velocities cause a strong solute variation in the melt, whence the defects are incorporated into the crystals in a random fashion. This is exactly what is observed in space grown crystals. Inspection of these results clearly indicates that the applied magnetic field can be applied effectively to suppress the spiking velocities, thereby reducing the variation of the concentration field, as one might have deduced from the single frequency simulations discussed above. The analysis of the computed results suggests that the applied magnetic field does not affect influence the solid-liquid interface. However, it substantially suppresses the concentration variation along the interface (see Figure 9). It is noteworthy that with a moderate magnetic field (0.5 Tesla), the concentration non-uniformity along the interface is almost entirely smoothed out.

V. Work In Progress

The work in progress involves extensive experimental measurements and numerical simulations to obtain more information that will help to enhance our fundamental understanding of magnetic damping effects on g-jitter induced flow and solidification phenomena in space processing systems and to help design damping facilities for microgravity applications. Numerical simulations will be continued to study magnetic damping of g-jitter flows and solutal striation and to quantify the effects of the field strength and direction, and the g-jitter frequency, orientation and amplitude, on the convective flows and solutal distribution and evolution in solidification systems. 3-D model for solidification phenomena is being developed, which will allow us to address both spatial and temporal effects more accurately. Ground-based measurements of oscillating flows and their effects on solidification will be conducted in the physical. The physical measurements will be compared with the numerical model predictions.

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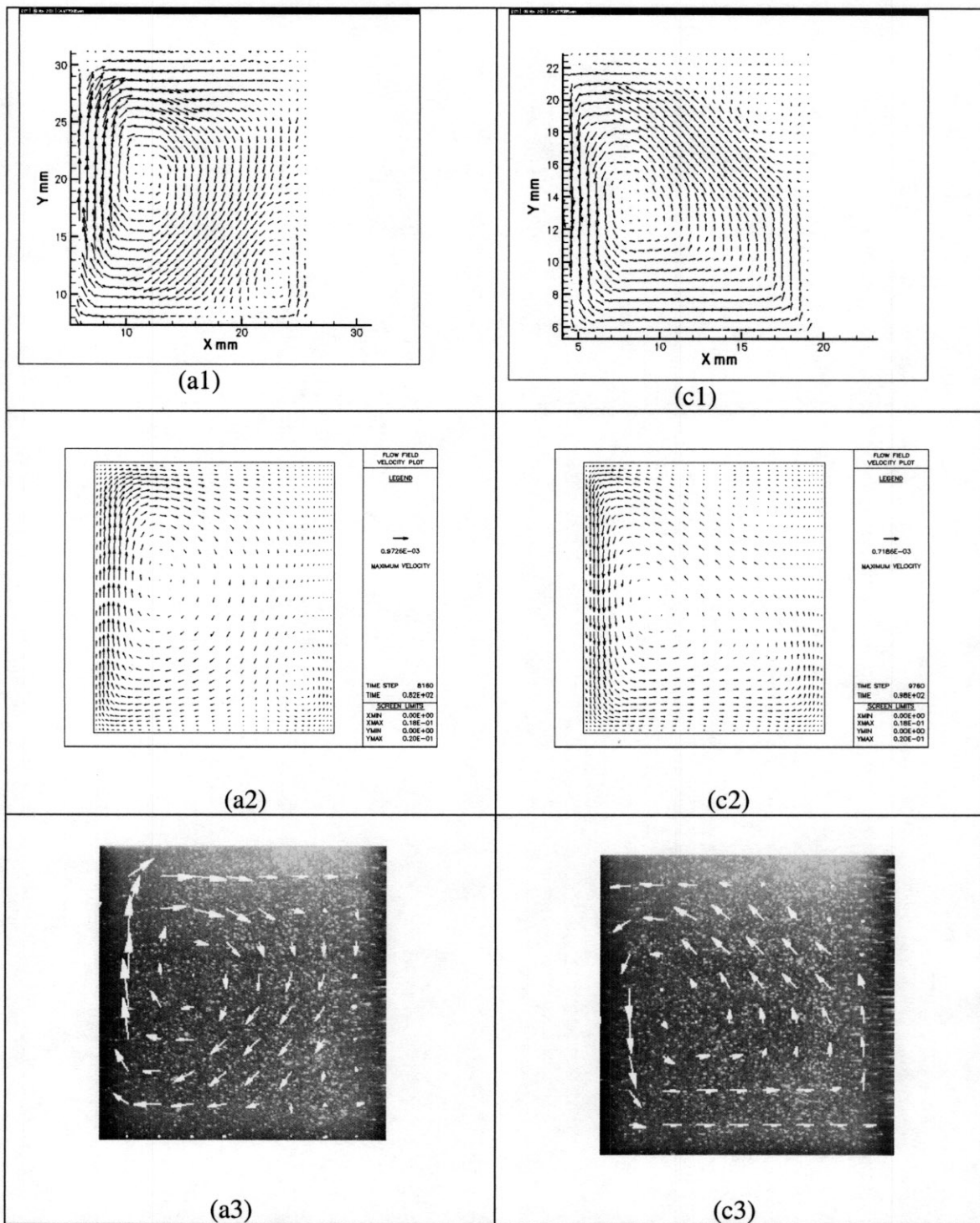


Figure 2. Oscillation of velocity fields driven by an oscillating temperature gradient within one thermal cycle, as measured by the PIV system and computed by numerical models. Frequency is 0.025Hz. (a1, c1,) are experimental results, (a2, c2) are numerical simulations and (a3, c3) are images directly from CCD camera.

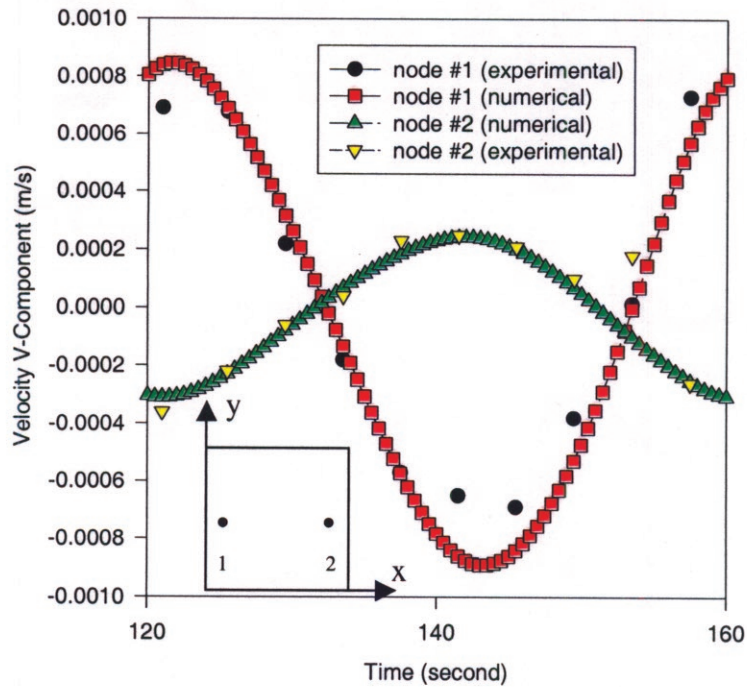


Figure 3. Comparison of measured and calculated velocity components at two locations in the testing cavity for the oscillation frequency of 0.025Hz. Coordinates of node #1 are ($x=0.0019$, $y=0.0105$) and coordinate of node #2 is (0.01601, 0.0105), all measured from the lower corner of the cavity.

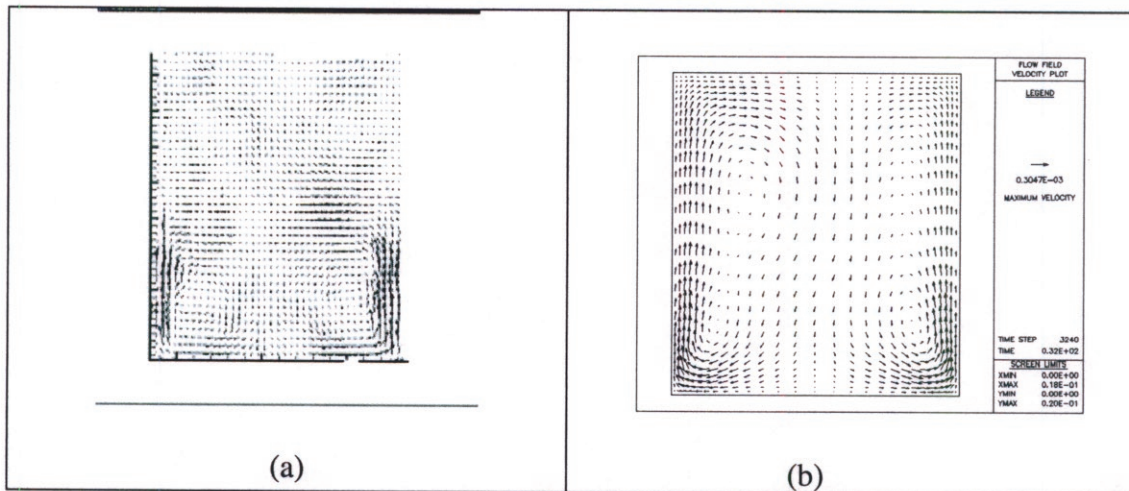


Figure 4. Experimentally measured and computed velocity field as induced by an oscillating temperature field with a frequency of 0.1Hz. (a) measured and (b) calculated.

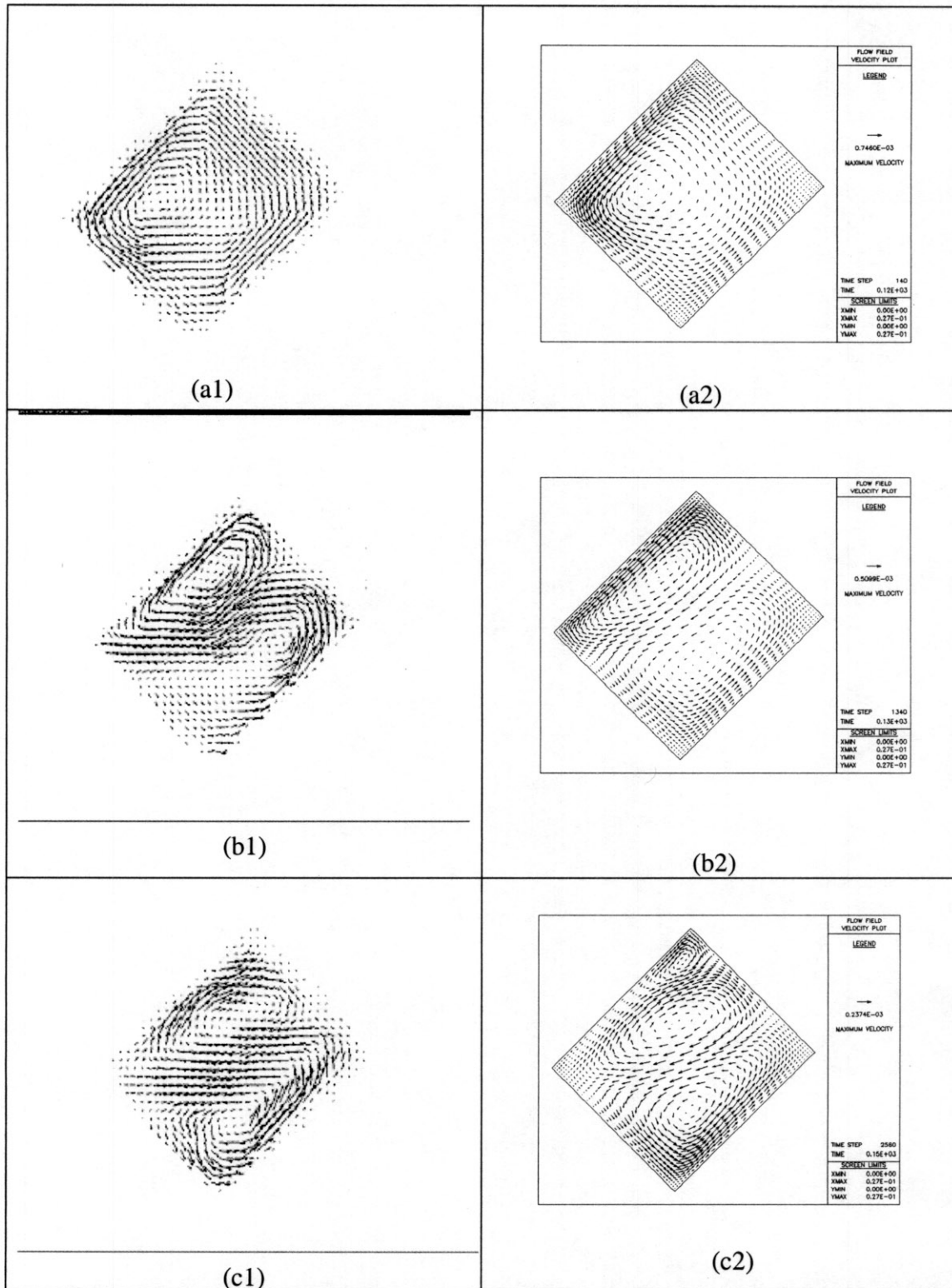


Figure 5. Comparison of transient development of oscillating velocity profiles measured by the PIV system and by the finite element model for the configuration tilted at 45° . The applied frequency is 0.025 Hz and the hot wall is on top. (a1, b1, c1) are measured and (a2, b2, c2) are numerical results.

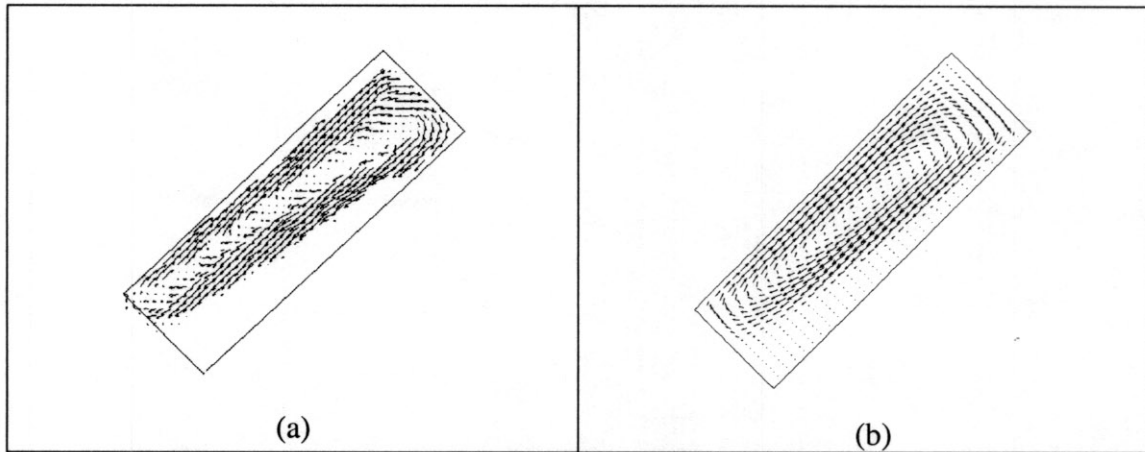


Figure 6. Comparison of measured (a) and calculated fluid field during solidification of SCN with cavity 45° tilted. Gravity points downward. The temperature of left tilt wall is 330.65 K and that at right is 335.05 K. $U_{\max}$ of (c) is 0.7631 mm/s and $U_{\max}$ of (d) is 0.6908 mm/s.

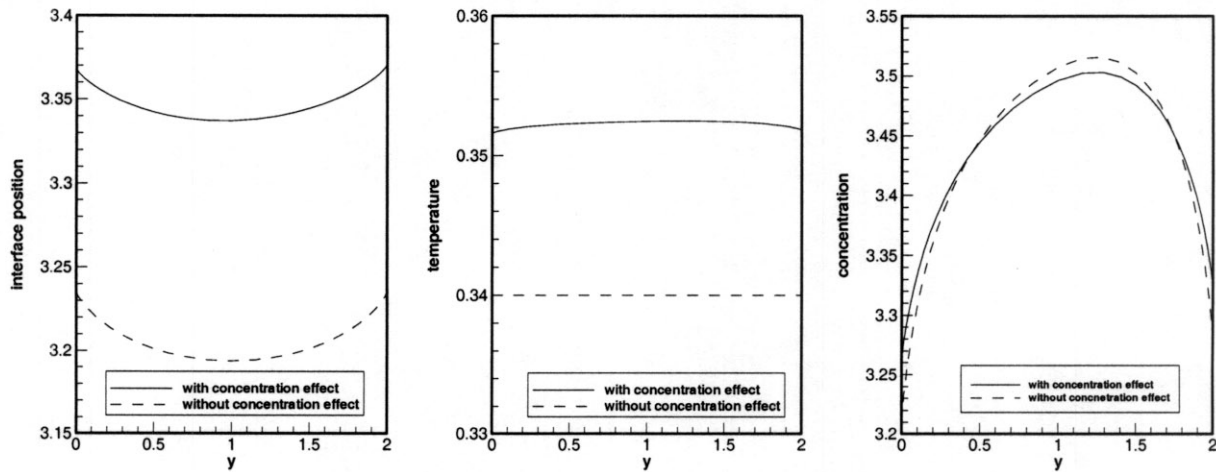


Figure 7. Dependency of interface position on concentration striation along the interface obtained from 2-D solidification model: (a) the interface positions, the temperature and concentration distributions along the growth interface of the steady cases with and without concentration effect respectively. Detailed conditions used for calculations are given in [15].

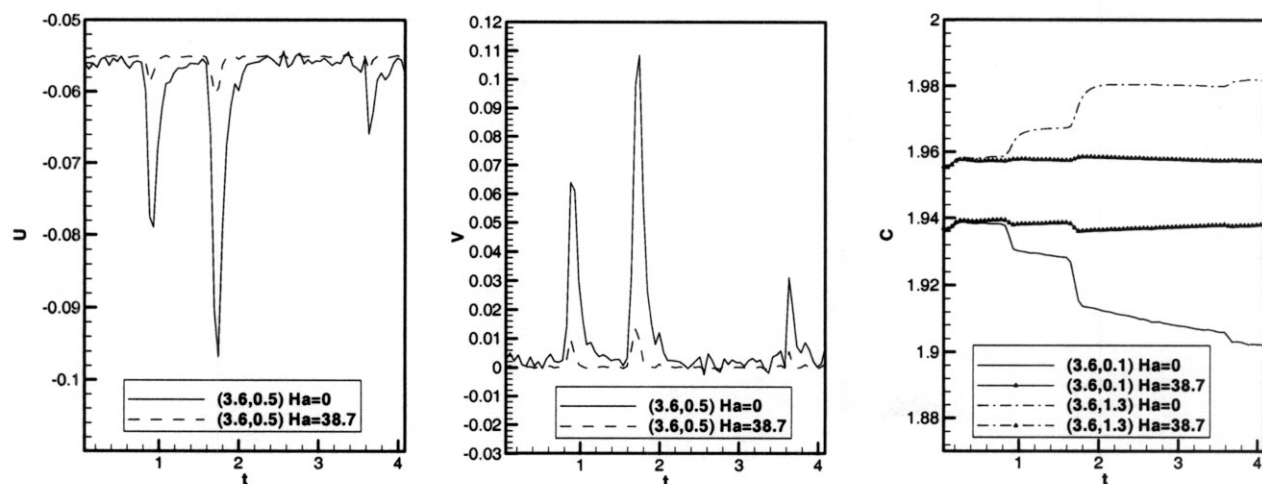


Figure 8. The effects of the magnetic field on the velocity and concentration oscillation caused by real g-jitter data at selected points in the melt near the growth front (a) $x=3.6$, $y=0.5$ (b) $x=3.6$, $y=0.5$ (c) $x=3.6$, $y=0.1$ and $x=3.6$, $y=1.3$. Parameters used for calculations are given in [15].

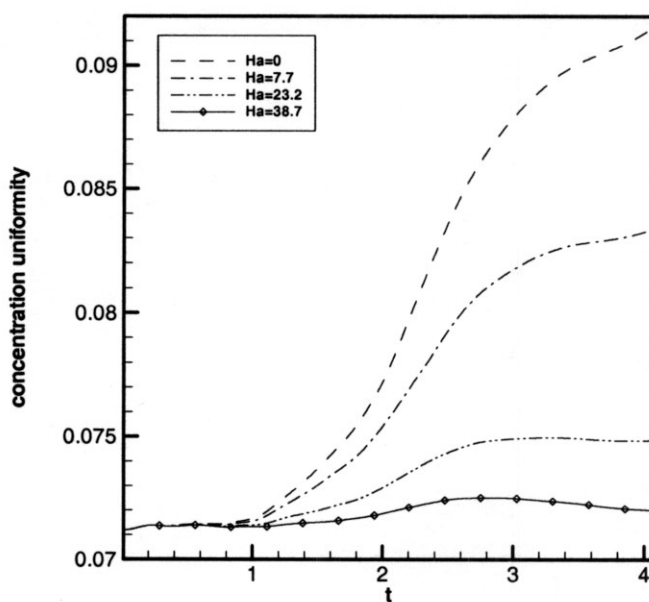


Figure 9. The effect of the magnetic field on the time evolution of the concentration uniformity along the growth interface caused by the real g-jitter. Detailed parameters for calculations are given in [15].

MODELS OF MASS TRANSPORT DURING MICROGRAVITY CRYSTAL GROWTH OF ALLOYED SEMICONDUCTORS IN A MAGNETIC FIELD

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Alloyed semiconductor crystals, such as germanium-silicon (GeSi) and various II-VI alloyed crystals, are extremely important for optoelectronic devices. Currently, high-quality crystals of GeSi and of II-VI alloys can be grown by epitaxial processes, but the time required to grow a certain amount of single crystal is roughly 1,000 times longer than the time required for Bridgman growth from a melt. Recent rapid advances in optoelectronics have led to a great demand for more and larger crystals with fewer dislocations and other microdefects and with more uniform and controllable compositions. Currently, alloyed crystals grown by bulk methods have unacceptable levels of segregation in the composition of the crystal. Alloyed crystals are being grown by the Bridgman process in space in order to develop successful bulk-growth methods, with the hope that the technology will be equally successful on earth. Unfortunately some crystals grown in space still have unacceptable segregation, for example, due to residual accelerations. The application of a weak magnetic field during crystal growth in space may eliminate the undesirable segregation. Understanding and improving the bulk growth of alloyed semiconductors in microgravity is critically important. The purpose of this grant is to develop models of the unsteady species transport during the bulk growth of alloyed semiconductor crystals in the presence of a magnetic field in microgravity. The research supports experiments being conducted in the High Magnetic Field Solidification Facility at Marshall Space Flight Center (MSFC) and future experiments on the International Space Station.

For alloyed semiconductors, the density differences due to compositional variations in the melt are very large. In germanium-silicon (GeSi), for example, the mole fraction of germanium may vary from 0.95 in the melt which has not yet received any rejected germanium to 0.99 near the interface, and this compositional difference corresponds to a density difference of nearly 300 kg/m³. In a frequently used extension of the Boussinesq approximation, the melt density is assumed to vary linearly with both the temperature and mole fraction of either species. In this approximation, the magnitudes of the density difference and of the resultant buoyant convection associated with the temperature variation or with the compositional variation are characterized by $\beta_T(\Delta T)_0$ and $\beta_C C_0$, respectively, where β_T and β_C are the thermal and compositional coefficient of volumetric expansion, while $(\Delta T)_0$ and C_0 are the characteristic radial temperature difference and the initially uniform mole fraction of the species, i.e. of silicon in the GeSi melt. For GeSi with $(\Delta T)_0=10$ K and $C_0=0.02$, the characteristic ratio of the buoyant convection driven by thermal variations to that driven by compositional variations is $\beta_T(\Delta T)_0/\beta_C C_0=0.2$. While the thermally-driven buoyant convection is probably not negligible, particularly far from the crystal-melt interface where compositional variations are small, the compositionally-driven buoyant convection or soluto-convection is dominant particularly near the interface.

Keywords: crystal growth, magnetic fields, modelling

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During the Bridgman growth of alloyed semiconductor crystals, the application of magnetic fields have shown great promise. For example, Watring and Lehoczky [1] have shown that the radial variation between the maximum and minimum concentrations can be decreased by more than a factor of three with the application of a 5 T magnetic field, arising because the magnetic field retards the sinking of the heavier melt to the center of the ampoule, resulting in less radial segregation. Ramachandran and Watring [2] reported a reduction in the radial segregation in all of their samples which were grown in a magnetic field.

The numerical treatment of transient species transport is difficult because (1) there are extreme differences between the time scales for the diffusions of internal energy, momentum and species, and (2) there are thin species-diffusion or viscous boundary layers for every value of the magnetic field strength. Therefore, the simultaneous time integration of the full Navier-Stokes, internal energy, and species transport equations must always have a very fine spatial grid and a very small time step so that simulating the entire crystal growth process is challenging. Our models involve the use of asymptotic models, which complement the numerical solutions of the full equations, in order to reduce the number of computations that are needed to accurately treat the entire growth process. Our simulations provide physical insight into the transport processes and can be used to systematically search over all possible combinations of controllable process parameters in order to determine the optimal processes which minimize segregation in the crystal.

To date, we have developed models [3,4] which treat the thermally-driven and compositionally-driven buoyant convections or solutal convection during the Bridgman or vertical gradient freezing growth alloyed semiconductor crystals with various orientations of an externally-applied steady magnetic field. The primary objective of this grant is to develop models which investigate the effects of the microgravity environment on segregation in the alloyed crystal grown in a magnetic field. Future research will be focused on applying our methods to treat solutal convection during the vertical gradient freezing of alloyed semiconductor crystals in a magnetic field in space. The effects of all three components of the residual acceleration, namely, the steady (DC) acceleration, g-jitters and spikes, eventually need to be investigated. The models would involve using asymptotic approximations which are appropriate for the reduced convective flows in microgravity and for the magnetic fields that will be used on the International Space Station.

Other research projects which have been supported by this grant include analytical and numerical modelling of (1) melt motions during floating-zone growth of high-purity silicon crystals in steady and rotating magnetic fields [5,6], (2) dopant transport during horizontal Bridgman growth of semiconductors in steady magnetic fields [7-9], and (3) dopant transport during liquid-encapsulated growth of compound semiconductor crystals in a magnetic field [10-14].

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NOVEL MICROSTRUCTURES FOR POLYMER-LIQUID CRYSTAL COMPOSITE MATERIALS

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I. Introduction

An understanding of the factors that control the orientation of liquid crystal (LC) molecules at interfaces is of great scientific as well as practical interest. The behavior of liquid crystals at interfaces is key to the performance of current and proposed optical devices such as flat panel displays, switchable light panels, and photonic band gap materials for optical beam steering. In flat panel liquid crystal displays, the grey scale contrast is controlled by the “pre-tilt angle”, which is the out-of-plane angle between the LC molecules and the inner surface of the display window [1]. The pre-tilt angle varies widely among different liquid crystal-forming materials, and depends in a subtle and unknown way upon the chemical structure of the molecules. This means that little guidance can be given to chemists in their attempts to synthesize new types of liquid crystals. Efforts to exploit the anisotropic optical properties of liquid crystals in switchable light panels has been pursued in the context of the so-called polymer dispersed liquid crystals (PDLCs), biphasic materials in which micron-sized droplets of minority phase liquid crystals are dispersed in a polymer matrix [2]. Recently, we have proposed that a novel family of polymer/liquid crystal composite materials formed under microgravity conditions may be more suitable, namely dispersions of polymer colloidal particles in liquid crystal media (liquid crystal dispersed colloids, or LCDCs). For both PDLCs and LCDCs, a significant volume fraction of the materials is associated with the interfacial region between the two phases. Here again control over the polymer/liquid crystal interface is key to the optimization of electro-optic properties.

These considerations have led us to adopt a coordinated experimental and molecular simulation approach to the study of liquid crystals at interfaces. In order to predict the effect of chemical structure on interfacial behavior, we use the powerful computational technique of molecular dynamics simulations [3]. In this technique, one chooses *a priori* a coarse-grained molecular model for the liquid crystal, incorporating values for important liquid crystal parameters such as molecular shape and flexibility. For a given molecular model, the classical equations of motion are rigorously solved to obtain the phase diagram and the interfacial properties. In our approach, we fine-tune the molecular model by comparing the interfacial properties obtained from the simulations with experimental measurements of the surface tension. In this way we obtain an accurate molecular model for a given liquid crystal, which can then be used for intelligent design of LCDCs or PDLCs.

II. Background

A liquid crystal (LC) phase is an equilibrium state of matter with a degree of molecular order intermediate between that of a crystalline solid and that of an isotropic liquid [2]. A number of different liquid crystal

Keywords: liquid crystals, surface tension, molecular dynamics, interfaces, microstructure, new research

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phases have been identified, two of which are sketched in Figure 1. A crystalline solid has long range orientational order, and long range translational order in all three dimensions. The molecules in an isotropic liquid, by definition, have no long range orientational or translational order. In a smectic A liquid crystalline phase, the molecules have long range orientational order and one-dimensional long range translational order. In a nematic LC phase, the molecules have long range orientational order but no long range translational order.

For many but not all liquid-crystal forming materials, the following sequence of phases can be observed by heating the material at constant external pressure: crystal, smectic, nematic, isotropic liquid. This sequence of phases is consistent with the typical phase diagram (pressure vs. temperature) sketched in Figure 2 [4]. However, note that this phase diagram exhibits a crystal/nematic/isotropic triple point at a pressure value denoted P_{NI^*} . Hence for pressures below P_{NI^*} , no liquid crystalline phases can be observed at any temperature. Since liquid crystals are used in electro-optic devices at atmospheric pressure, we have the obvious practical requirement on new liquid crystals that $P_{NI^*} < 1$ atm. However, as far as we know, there have been no previous molecular simulation studies of liquid crystals at pressures as low as one atmosphere. Hence the subtle details of chemical structure necessary to obtain $P_{NI^*} < 1$ atm are largely unknown.

III. Specific Aims

To be concise, the specific aims of this research project are given in the following list (not in chronological order):

1. To determine the subtle molecular details (e.g. degree of shape asymmetry or flexibility) needed in molecular dynamics computer simulations in order to observe liquid crystalline phases at atmospheric pressure. The simulations will employ so-called “coarse-grained” molecular models without atomistic detail, because liquid crystal models with atomistic detail are too computationally expensive for simulations of interfaces.
2. To fine tune the molecular model for a given liquid crystal by comparing experimental measurements of the liquid crystal free surface (i.e. surface tension vs. temperature) to the simulation predictions.
3. To extend the validated molecular simulation program to interfaces that are more difficult than free surfaces to study experimentally, such as the interface between a liquid crystal and a colloidal polymer particle.
4. To perform preliminary proof-of-principle tests on a novel type of polymer/LC composite that is a potential photonic band gap material, namely liquid crystal dispersed colloids (LCDCs).

IV. Development of the Molecular Simulation Model

In nature, materials that exhibit liquid crystalline phases are almost always composed of rodlike or disc-shaped molecules [2]. Molecular simulation studies of “hard” ellipsoids (i.e., without any attractive intermolecular interactions) have confirmed that molecular asymmetry is a requirement – liquid crystalline phases are not observed unless the molecular length-to-diameter ratio is at least 3 [5]. Molecular simulations based on hard molecular models do not predict that a liquid crystalline phase can be produced by melting the crystal, and thus cannot be used to model “thermotropic” liquid crystals used in device applications. Therefore the simplest plausible coarse-grained molecular model for a thermotropic liquid crystal is a rigid necklace of connected spherical beads (Figure 3). Each molecule contains eleven spherical beads and has a molecular aspect ratio of 6, with attractive Lennard-Jones interactions between beads in different molecules. We have used constant-pressure-molecular-dynamics simulations with the

Gibbs-Duhem integration method to map out much of the bulk phase diagram for the molecular model shown in Figure 3 [6]. This molecular model yields a smectic A phase, a nematic phase, and an isotropic liquid phase. However, the liquid crystalline phases disappear at low pressures; that is, $P_{NI^*} > 1$ atm. Thus this molecular model cannot be used to simulate LC free surfaces, or to simulate LC behavior in electro-optic devices at one atmosphere.

A more promising molecular model is sketched in Figure 4, the so-called “ellipsoid-shaped LC model”. This model has a similar aspect ratio, with eleven rigidly attached spherical beads (no flexibility), and Lennard-Jones attractive forces between beads in different molecules. However, in order to disrupt molecular packing in the crystal, we made the three central beads in a given molecule 50% larger in diameter than the neighboring beads. This somewhat subtle modification is sufficient to produce stable nematic phases at atmospheric pressure. Figure 5 shows molecular simulation results for the density vs. temperature (in reduced units) along the isobar $P = 1$ atm for the molecular model of Figure 4. When cooled from high temperatures in the gas phase, the model system exhibits an abrupt increase in density, indicative of a first order phase transition, when the reduced temperature reaches 1.8 (dimensional temperature $\cong 340$ K). A second phase transition is observed when the reduced temperature reaches about 1.3 (dimensional temperature $\cong 240$ K). These transition temperatures can be adjusted in future molecular models by varying the strength of the intermolecular potential. The molecular orientation order parameter S calculated from the simulations is approximately 0.7 for temperatures below 240 K, and approximately zero for temperatures above 240 K. This allows us to identify the phase formed below 240 K as *nematic*. Apparently this is the first stable nematic phase that has been observed at atmospheric pressure in molecular simulations. We are currently using the same molecular model to simulate liquid crystal free surfaces, for comparison to concurrent experimental measurements of liquid crystal surface tension. The experimental results will be used to adjust the parameters of the molecular model.

V. Liquid Crystal Dispersed Colloids (LCDCs)

A photonic band gap (PBG) material is a periodic array of colloidal particles or other dielectric elements with periodicity comparable to the wavelength of light [7]. Due to the three-dimensional, periodic variation in the dielectric constant, PBG materials can be used to controllably prohibit propagation of electromagnetic radiation in a specified frequency band. Potential uses for such materials include optical filters, waveguides and numerous other devices in optical telecommunications. Experiments have shown that the forces present between colloidal particles in a liquid crystal solvent tend to order the particles in periodic chains [8]. Therefore we hypothesize that an LCDC, a dispersion of colloidal polymer particles in a liquid crystal solvent, may form a highly regular and novel PBG material under microgravity conditions.

For proof-of-principle tests in ground-based experiments, we have developed the process sketched in Figure 6 for producing synthetic opals, which are ordered arrays of silica particles. Suspensions of colloidal silica particles in water will self-assemble into ordered arrays under the influence of gravity, but the process is very slow, taking 5-7 months. Using a centrifuge, we have produced synthetic opals with comparable ordering parameters in just over three hours. In the future, the water within the voids of the silica lattice will be replaced with an appropriate liquid crystal solvent, and the photonic band gap will be measured. It should be possible to manipulate the photonic band gap of such a material by using an electric field to switch the alignment of the liquid crystal molecules.

A better understanding of the forces between colloidal particles dispersed in a liquid crystal medium might allow us to manipulate the periodicity of an ordered LCDC by varying the LC solvent. A simpler

experimental system for studying these forces is a water-in-thermotropic liquid crystal microemulsion [9]. We have prepared such a microemulsion by mixing together a small amount of water and surfactant with a thermotropic liquid crystal at elevated temperatures, and then slowly cooling the system. The thermotropic liquid crystal, 4-pentyl-4'-cyanobiphenyl (5CB) undergoes a phase transition from an isotropic liquid to a nematic liquid crystal at 35.3 °C. Hence the mixture spontaneously forms a microemulsion as the temperature is lowered. Light scattering experiments, electric birefringence measurements, and differential calorimetry is being used to investigate the forces between the sub-micron sized water droplets.

VI. Conclusions and Future Directions

We have identified a coarse-grained molecular simulation model that exhibits a stable nematic liquid crystalline phase at atmospheric pressure. Such a model can be used to guide synthetic chemists by predicting the shape of the liquid crystal molecule that gives the best grey-scale contrast in liquid crystal displays. In future work we plan to refine the liquid crystal molecular model by using experimental results to adjust the model parameters, and by adding features like “floppy tails” which are often present in real liquid crystal molecules.

Two preliminary versions of a LCDC have been prepared: a synthetic opal with a liquid crystal in the voids of the silica lattice; and a microemulsion of water droplets in a liquid crystal matrix. Our long range goal is a colloidal crystal in a liquid crystal solvent with a controllable lattice spacing.

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Figure 1-The various phases of liquid crystals

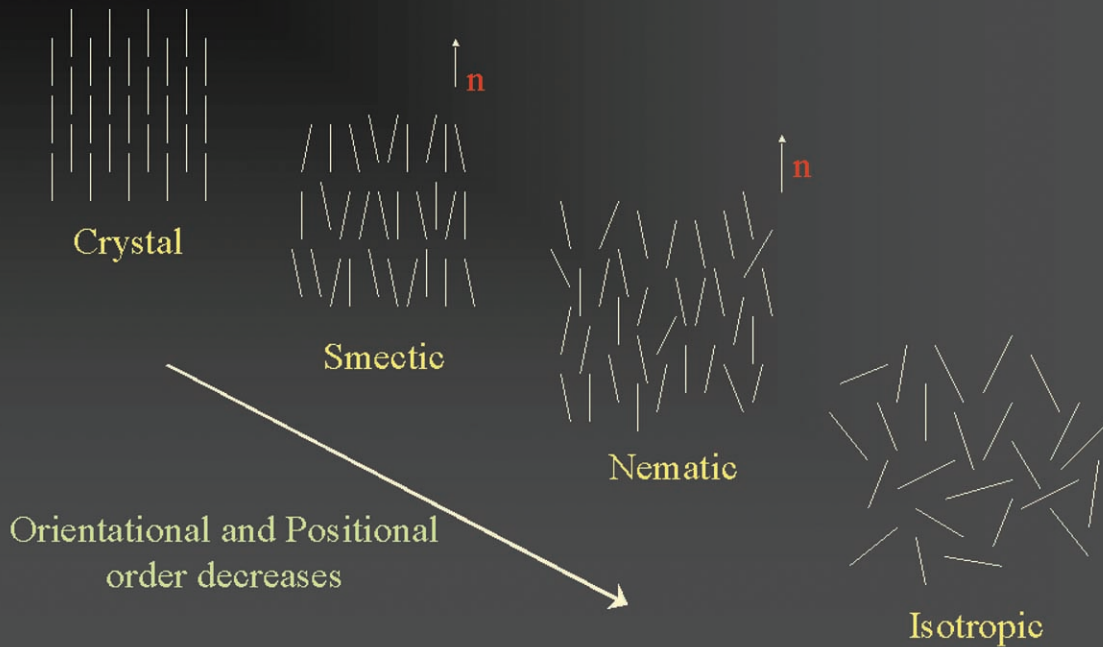


Figure 2 - Typical phase diagram – No Liquid Crystals at $P < P_{NI^*}$

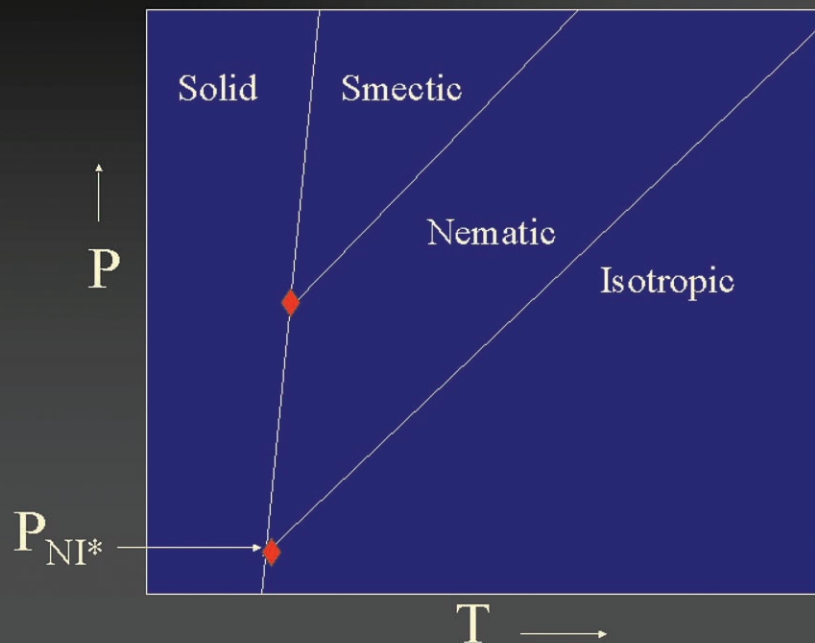


Figure 3 - Simple Bead Necklace Liquid Crystal Molecular Model

- ❖ 11 beads
- ❖ Equally spaced
- ❖ Rigid molecule
- ❖ $L/D \sim 5$

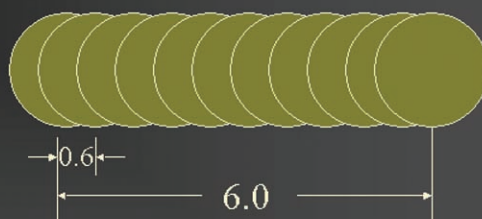


Figure 4 - Ellipsoid shaped liquid crystal molecular model

- ❖ 11 beads
- ❖ Bigger beads - σ_{11}
- ❖ Smaller beads - σ_{22}
- ❖ $\sigma_{11} / \sigma_{22} = 1.54$
- ❖ Simulations only at 1 atm
- ❖ Density, Orientational order and positional order –Temperature

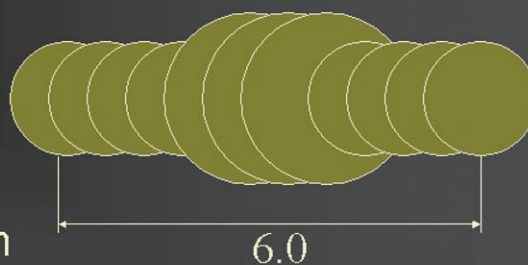


Figure 5 - Density as function of temperature for ellipsoid shaped liquid crystal at fixed pressure of 1 atmosphere

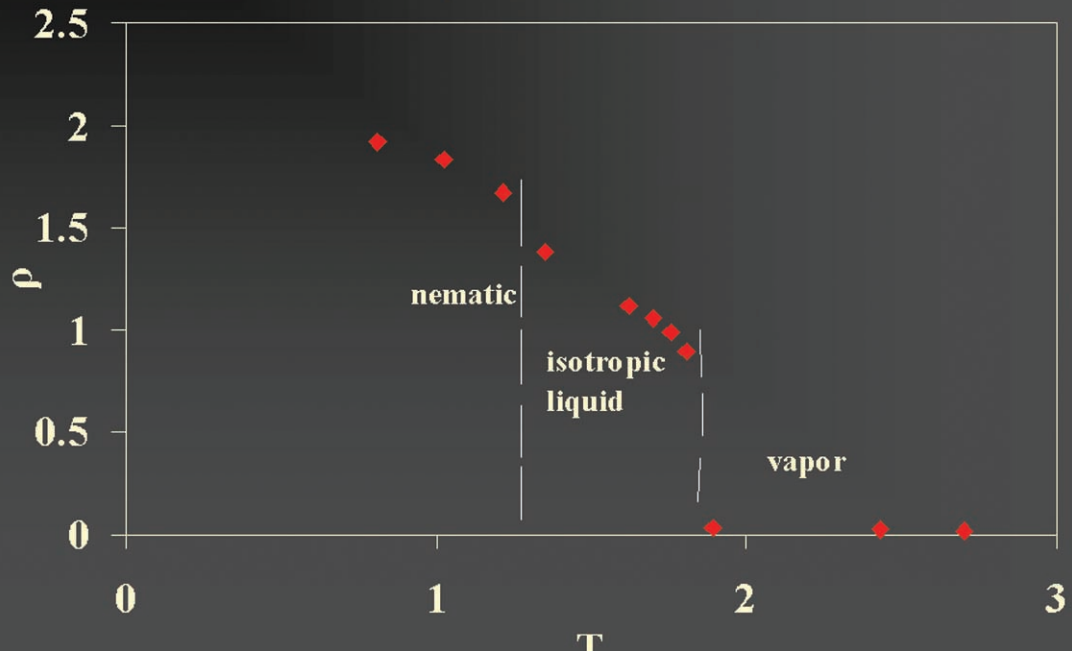
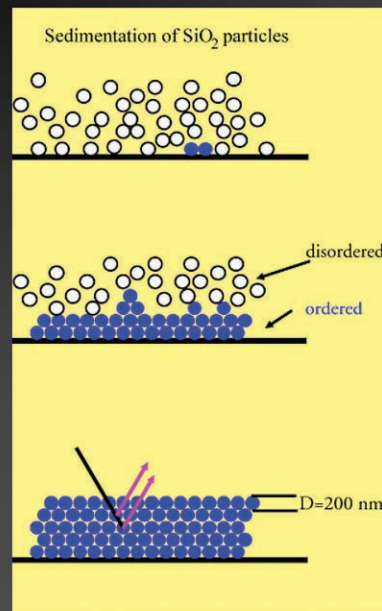


Figure 6: Photonic Bandgap Material Formed by Self-assembly in Liquid Crystal Medium



CO₂ ACQUISITION MEMBRANE (CAM)

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The objective of CAM is to develop, test, and analyze thin film membrane materials for separation and purification of carbon dioxide (CO₂) from mixtures of gases, such as those found in the Martian atmosphere. The membranes are targeted toward *In Situ Resource Utilization (ISRU)* applications that will operate in extraterrestrial environments and support future unmanned and human space missions. A primary application is the Sabatier Electrolysis process that uses Mars atmosphere CO₂ as raw material for producing water, oxygen, and methane for rocket fuel and habitat support. Other applications include use as an inlet filter to collect and concentrate Mars atmospheric argon and nitrogen gases for habitat pressurization, and to remove CO₂ from breathing gases in *Closed Environment Life Support Systems (CELSS)*.

CAM membrane materials include crystalline faujasite (FAU) zeolite and rubbery polymers such as silicone rubber (PDMS) that have been shown in the literature and via molecular simulation to favor adsorption and permeation of CO₂ over nitrogen and argon. Pure gas permeation tests using commercial PDMS membranes have shown that both CO₂ permeance and the separation factor relative to other gases increase as the temperature decreases, and low ΔP_{CO_2} favors higher separation factors. The ideal CO₂/N₂ separation factor increases from 7.5 to 17.5 as temperature decreases from 22 °C to -30 °C. For gas mixtures containing CO₂, N₂, and Ar, plasticization decreased the separation factors from 4.5 to 6 over the same temperature range. We currently synthesize and test our own Na⁺ FAU zeolite membranes using standard formulations and secondary growth methods on porous alumina. Preliminary tests with a Na⁺ FAU membrane at 22 °C show a He/SF₆ ideal separation factor of 62, exceeding the Knudsen diffusion selectivity by an order of magnitude. This shows that the membrane is relatively free from large defects and associated non-selective (viscous flow) transport mechanisms.

The Membrane Test Facility (MTF) has been developed to measure membrane permeance over a wide range of temperature and pressure. The facility uses two volume compartments separated by the membrane that are instrumented to measure temperature, delta pressure across the membrane, and gas composition. A thermal shroud supports and encloses the membrane, and provides temperature control. Methods were developed to determine membrane permeance using the first order decay of the pressure difference between the sealed compartments, using the total pressure for pure gases, and partial pressure of each species in gas mixtures. The technique provides an end-to-end measurement of gas permeance that includes concentration polarization effects. Experiments have shown that in addition to membrane permeance properties, the geometry and design of associated structures play an important role in how membrane systems will function on Mars.

Keywords: zeolite, membrane, ISRU, Sabatier Electrolysis

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DIFFUSION PROCESSES IN MOLTEN SEMICONDUCTORS (DPIMS): FLIGHT RESULTS FROM THE STS-94/MSL-1R SPACELAB MISSION

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The Diffusion Processes in Molten Semiconductors (DPIMS) investigation was a three-part program that sought to:

- 1) Provide purely diffusive experimental measurements of the isothermal diffusion coefficients of gallium (Ga), antimony (Sb) and silicon (Si) in molten germanium (Ge) with sufficient accuracy and precision to:
 - a) Differentiate between model predictions of the temperature dependence.
 - b) Determine the effect of dopant size and type.
 - c) Determine if a “wall effect” was present.
 - d) Provide input to continuum model development.
 - e) Provide input to atomistic model development.
- 2) Develop a 2-dimensional, fully time dependent continuum numerical model of the germanium diffusion column, shear cell, cartridge and furnace for both earth-based and space-based experiments which accurately predicted the measured concentration profile as a function of distance in the diffusion column.
- 3) Develop an atomistic model that accurately predicts:
 - a) The purely diffusive isothermal diffusion coefficient of a dopant in a molten semiconductor.
 - b) The temperature dependence of the dopants in molten semiconductors.
 - c) Developed new empirical potentials useful for predicting other transport properties in molten semiconductor systems.

The efforts of the last two years have yielded outstanding results from all three parts of the DPIMS program. Despite numerous off nominal conditions, several of the diffusion experiments that were run on the MSL-1R Spacelab mission have yielded reliable diffusion coefficients. These diffusion coefficients are unexpectedly higher than those predicted from the Stokes-Einstein equation as well as those predicted by *ab-initio* computer modeling efforts. These diffusion coefficients were calculated using the ‘long-time’ solution to Fick’s second law from the measured concentration versus distance profile of the diffusion column. The concentration measurements were determined using Inductively Coupled Plasma- Mass Spectrometry (ICP-MS). A newly developed 3-parameter iterative solution technique combined with Monte Carlo simulations has allowed for a statistically accurate estimate of the error for these diffusion coefficients to be made.

Keywords: flight samples, diffusion, dopants, semiconductors, modeling

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NEUTRON PRODUCTION MEASUREMENTS FROM SHIELD MATERIALS

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Astronauts who spend months and years traveling long distances in spacecraft and working on other planets will be subjected to high-energy radiation of galactic and solar origin without the protection of the Earth's thick (one writer has called it buff) atmosphere and magnetic field. The lack of natural protection will allow high-energy cosmic ray particles and solar protons to crash directly into relatively thin spacecraft walls and planetary atmospheres producing energetic secondary particles in these collisions.

A substantial fraction of these secondaries will be neutrons that carry no electric charge and, consequently, are difficult to detect. At sea level on Earth the remaining neutrons are the result of many generations of collisions producing a spectrum with a large low energy component. These neutrons do contribute to the natural background radiation dose seen by humans amounting to hundreds of millirems per year.

In the International Space Station or on the surface of Mars, the secondary neutrons will be the result of only one or two generations of interaction due to the thinner (about a factor of 20 compared to the Earth's atmosphere) walls or atmosphere, have considerably more energy and penetrate deeply into the human body. In addition, neutrons are substantially moderated by hydrogenous material such as water. A significant fraction of the water exists in the astronaut's body. Therefore, the neutron can not only penetrate more deeply into the body, but also be stopped there and deposit all or a significant fraction of its energy as radiation dose in organs such as the liver, spleen, kidney, etc. We hypothesize that the risk of serious cancers will be increased for the exposed humans.

The portable, real time neutron spectrometer being developed by our team will monitor the environment inside spacecraft structures and on planetary surfaces. Activities supported by this grant will evaluate the neutron environment behind candidate spacecraft materials at accelerator facilities. These experiments will enable engineers to choose the structure materials that minimize the production of secondary neutrons. With the information that the neutron energy spectrometer produces, scientists and doctors will be able to assess the increased risk of cancer and develop countermeasures.

A 5 mm thick lithium drifted silicon detector system for an engineering prototype spectrometer funded by NASA/NSBRI has been tested and calibrated with mono-energetic neutron beams at the Los Alamos Neutron Science Center (LANSCE) and the Columbia University Radiological Accelerator Research Facility (RARAF). While at LANSCE we also conducted experiments on the effectiveness of polyethylene in shielding high-energy neutrons. A prototype spectrometer consisting of the thick silicon detector for high energy neutrons and a helium 3 gas tube detector for low energy neutrons was flown at 40,000 feet altitude in fighter aircraft from NASA Dryden in 2001 as an engineering test to verify flight capability.

Keywords: neutrons, shielding, thick target collisions, radiation

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Balloon flights are planned for 2002 and 2003 at altitudes that should yield downward high-energy neutron spectra similar to those to be experienced on the surface of Mars.

For ground based neutron shielding materials studies at proton and heavy ion beam accelerators we modified the proto-flight spectrometer to use a thin silicon transmission detector in the beam direction as a charged particle veto instead of the bulky CsI tube that surrounds the thick silicon detector to be used in flight. The primary purpose of the instrument is to determine the neutron spectrum produced behind shielding material due to nuclear reactions between the incident particle beam and the shielding material. This task is accomplished by recording the non-vetoed neutron energy deposition events in the thick Lithium Drifted Silicon (SiLi) detector and using a response function inversion method to de-convolve the most probable incident neutron spectrum. The block diagram of this detector system is shown in Figure 1. The construction of this instrument dedicated to accelerator facility testing has been completed. An aluminum mounting frame to hold and position the detector system has also been fabricated. The detector system can be placed behind the shielding material at various distances near the beam axis and at small angles in the forward direction off the beam axis.

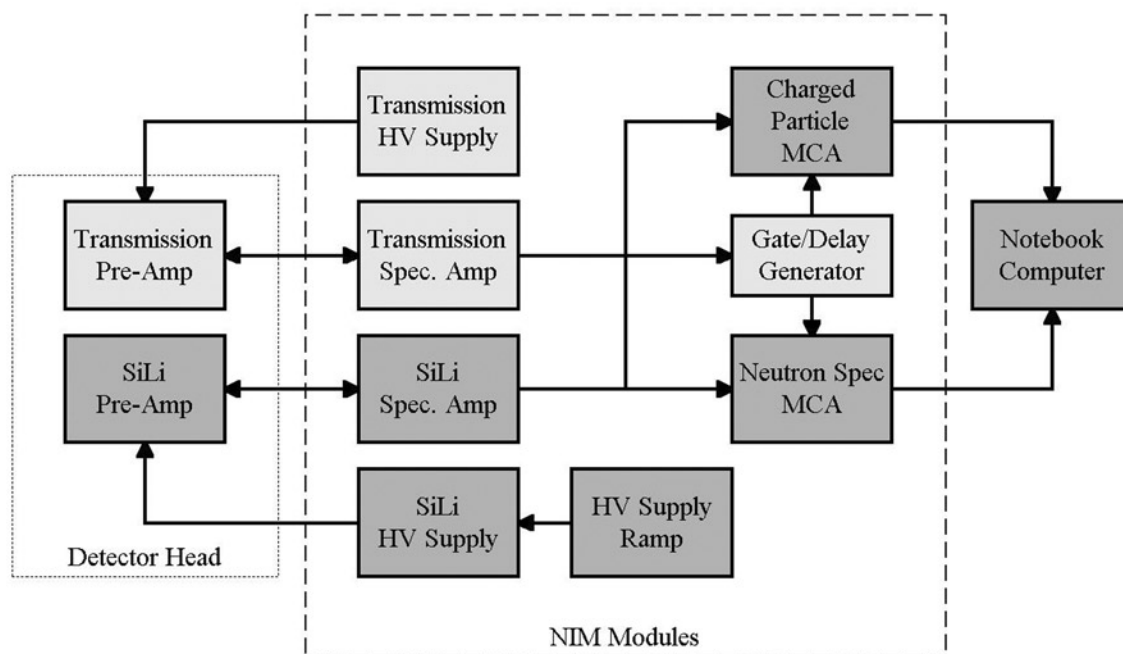


Figure 1: Shielding Materials Experimental Configuration showing the transmission and bulk solid state detectors mounted in tandem. The front transmission detector provides charged particle anticoincidence in the beam direction only.

Experimental characterization of this detector system with respect to its neutron detection efficiency and ability to discriminate against charged particles including calibration has been completed at Columbia RARAF and the results are shown in Figure 2. The smaller accelerator system gives results equivalent to those of the bulkier flight system.

Comparison of CsI and Si Stack Anti-Coincidence

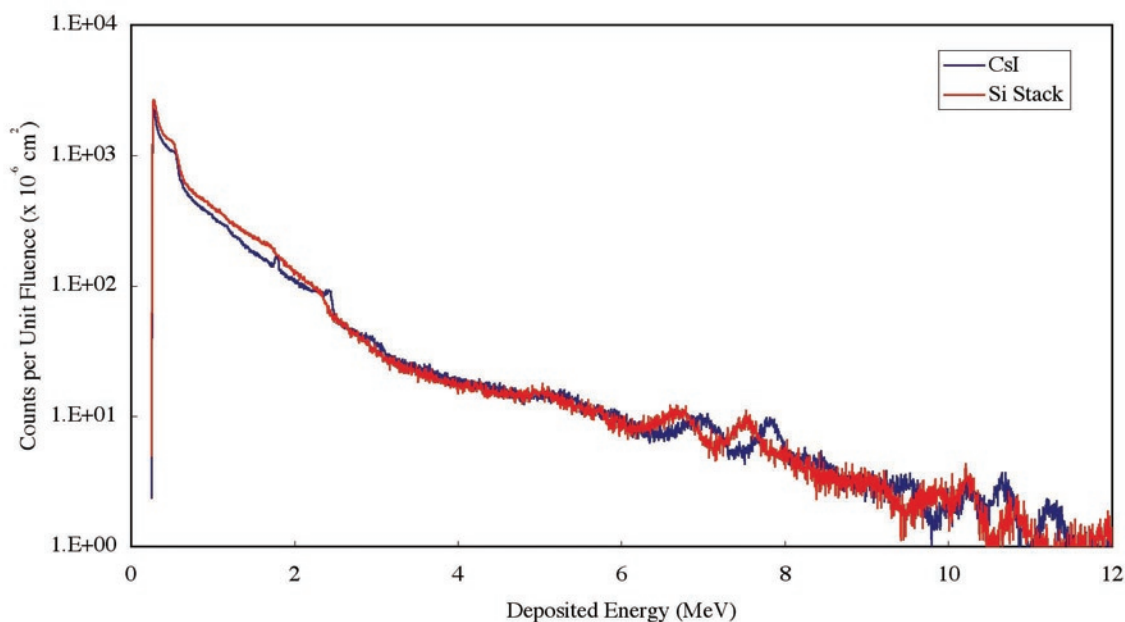


Figure 2: Comparison of CsI scintillator and silicon transmission anti-coincidence detectors and the counts per unit 14 MeV neutron fluence at Columbia RARAF. This comparison shows that the smaller detector system in Figure 1 gives the same results for neutron energy deposition spectra when the beam and anti-coincidence are unidirectional.

From the experiments at RARAF with 14 MeV neutrons and five shield thicknesses of polyethylene we have deduced the integral energy deposition spectra shown in Figure 3. The mostly parallel set of curves indicate that one needs 4", 2" of polyethylene to reduce the 7 MeV (half the incident neutron energy) depositions by factors of 3, 1.8 respectively. The results for energy depositions of 2 MeV are very similar. For polyethylene thicknesses of 1" or less the greatest reduction in neutron depositions is about 25%.

Similar results were obtained at LANSCE for 20-600 MeV neutrons as shown in Figure 4. In this case almost no reduction in neutron flux occurred for 2" of polyethylene and 4" was necessary to achieve a significant reduction (~a factor of 4.5).

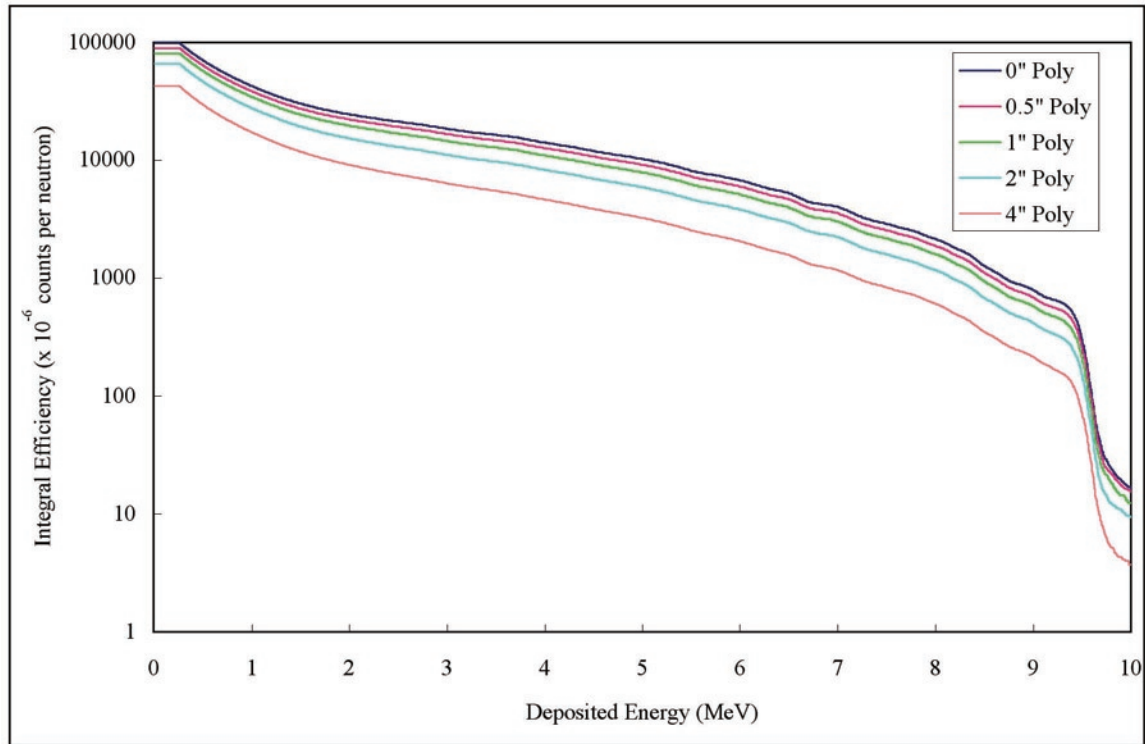


Figure 3: Integral Response Deposition Spectra due to 14 MeV neutrons incident on Polyethylene. The ordinate axis has been multiplied by 10^6 to make the exponents positive. From top to bottom the curves are for 0, 0.5, 1, 2, 4 inches of polyethylene.

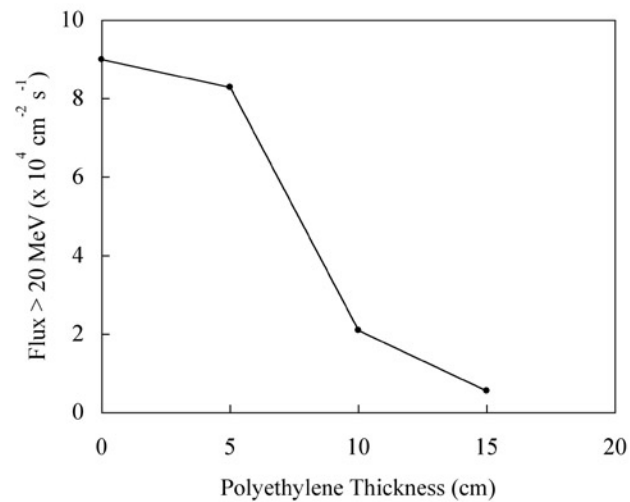


Figure 4: Polyethylene Shielding Effectiveness for High Energy Neutrons. The ordinate scale is integral flux > 20 MeV in units of $\text{cm}^{-2} \text{ sec}^{-1}$

Summary:

- 1) We have designed and fabricated a stack detector system consisting of a silicon transmission detector and a 5mm thick lithium drifted silicon detector. This system has the same charged particle anti-coincidence efficiency in the accelerator beam direction as our flight prototype has from a CsI crystal surrounding a thick lithium drifted detector as shown by experiments with 14 MeV neutrons. This system is available for radiation shielding material experiments.
- 2) From work supported by the National Space Biomedical Research Institute (NSBRI) we have developed and verified a de-convolution technique that calculates a most probable incident neutron energy spectrum from the deposited energy spectra measured by the 5mm thick silicon detector. A publication on this result is presently in the review cycle.
- 3) We find for fast and high-energy neutrons that four inches (10 cm) of polyethylene is necessary to make a significant reduction in the neutron flux. For the fast (10-20 MeV) neutrons a reduction of a factor of 3 was indicated while for the high-energy neutrons (20-600 MeV) a factor of 4.5 was determined.
- 4) We are planning to study neutrons produced in collisions of high-energy protons with prospective shield materials in the Fall of 2002. We will measure both the neutron spectra produced in these collisions and the shielding effectiveness of polyethylene for these same spectra.

CONTROLLED SYNTHESIS OF NANOPARTICLES USING STAR-BLOCK COPOLYMER NANOREACTORS

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Jinchuan Yang,¹ and Ji Ho Youk¹

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Abstract

To achieve complete control of nanoparticle properties, it is necessary to obtain samples that are as close to monodisperse as possible. Polymers such as linear and star-linked poly(styrene)-block-poly(2-vinylpyridine) generate micelles in low polarity solvents like toluene, which can be used as reactors for the preparation of nanoparticles. We have established reliable synthetic routes for the preparation of CdS, CdSe, and Au nanoparticles within block copolymer micelles and within star-block copolymers.

In a typical CdS preparation, a methanol solution of $\text{Cd}(\text{NO}_3)_2$ is added to the toluene solution of block copolymer, followed by the addition of Na_2S ($[\text{Cd}^{2+}]/[\text{S}^{2-}] = 0.6$) and thioglycerol in methanol. Thioglycerol is an auxiliary capping agent that improves both the stability and monodispersity of the CdS nanoparticles. The particles obtained through this method have mean sizes of 10 nm for preparations using linear block copolymers, and 25 nm with star block copolymers. The particles show strong quantum confinement as seen in the absorption and emission spectra. The absorption spectra also indicate particle stability in solution for a minimum of 3 months. The necessity of polymer nanoreactors for the preparation of high quality particles is demonstrated by the emission spectra of CdS nanoparticles prepared with homopolystyrene and linear or star-linked poly(styrene)-block-poly(2-vinylpyridine). The yield and quality of CdS particles is greatly reduced if homopolystyrene is used, resulting in a weaker, broader, and blue-shifted emission. *Both the emission spectra and TEM micrographs suggest that the star-linked block copolymer is superior for the preparation of high quality particles.* This is probably due to enhanced micelle stability and homogeneity.

We have also had great success in extending these synthetic routes to the preparation of CdSe and gold nanoparticles, where again the novel use of star-block copolymers is advantageous. In these cases, particles are prepared without the need of an auxiliary capping agent, which allows us to increase the concentration of reagents and the yield of the preparations. Furthermore, we have prepared gold nanoparticles in aqueous solution using a polyelectrolyte that possesses pendant reducing oligothiophene groups. Polyelectrolyte complex (PEC) with water-soluble terthiophene derivative was used for the reduction of HAuCl_4 to gold nanoparticles. A number of parameters including solution concentration, percentage of complexation, solvent, reaction time, etc. were investigated in order to determine the extent of the reduction and nanoparticle formation (size, size distribution, etc.). This technique opens the possibility of combining electro- and optically-active materials with metal nanoparticles prepared *in-situ*.

Keywords: nanoparticle, gold, cadmium sulfide, star-block copolymer

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In summary, we can reliably produce CdS, CdSe, and Au nanoparticles that are stable in solution for long times (at least three months). These particles are nano-sized (mean sizes typically 10-50 nm for semiconductors and as small as 4-8 nm for Au) and approximately spherical. The CdS and CdSe nanoparticles are very good emitters. Dilute solutions produce emissions clearly visible to the naked eye. The polydispersity is quite good, and the emission spectrum does not vary drastically with excitation wavelength. Thus, a major goal of this Earth-bound project has been achieved. The next step is to determine whether or not nanoparticle growth in a microgravity environment can further reduce the polydispersity of these materials.

Introduction

Nanoparticles of semiconductors and metals have been extensively studied in recent years due to their novel material properties which are greatly different from those of their bulk substances.¹ To achieve complete control of the properties of nanoparticles, it is necessary to prepare monodisperse particles with respect to size, shape, and internal structure. For example, the band gap of a semiconductor nanoparticle material is dependent on particle size and thus both its absorption and emission spectra are size dependent. A polydisperse semiconductor nanoparticle will show a broad emission spectrum, reflecting the overlap of multiple emission bands.²⁻⁵

During the past decade, many examples of synthetic methods using polymer materials have been developed, among which synthesis of nanoparticles in a polymer matrix is prominent.⁶⁻¹² Besides acting as a stabilizer, the use of a polymeric matrix as a medium for nanoparticle formation provides for processability, solubility and control of nanoparticle growth.⁶ Most of the methods are based on compartmentalizing the reagents to prepare nanoparticles using in situ reactions. Various types of polymer “nanoreactors” have been used for nanoparticle growth including block copolymer micelles,^{13,14} bulk block copolymers⁷⁻¹⁰ and dendrimers.^{15,16}

To overcome these drawbacks for the preparation of gold nanoparticles, PS-*b*-P2VP star-block copolymer architectures, physically resembling diblock copolymer micelles, can be used as a highly promising material in lieu of micelles.¹⁷ In this case, there is no more concern about the micelle instability with time and concentration because the core segments of the star-block copolymer are *covalently bound*. Furthermore, the star-block copolymer can be synthesized with a very narrow molecular weight distribution (MWD) and with a variety of macromolecular architectures and constitutions.¹⁸ In this case, nanoparticle synthesis can be confined within the core of the star-block copolymer compared to the core of a diblock copolymer micelle. This can be done by controlling the inner core polymer block length and constitution of the star. In this study, a PS-*b*-P2VP star-block copolymer was synthesized and gold and CdS nanoparticles were prepared within the core. The size distribution and long-term stability against aggregation of the gold nanoparticles were investigated.

Experimental

PS-*b*-P2VP star-block copolymers were synthesized anionically using butyllithium in tetrahydrofuran at -78 C. Linking was carried out using ethylene glycol dimethacrylate (EGDMA) (Fig. 1). To prepare gold nanoparticles, a 5 mg/mL solution of PS-*b*-P2VP star-block copolymer in dry toluene was mixed with three different concentrations, 0.1, 0.3, and 0.5 equiv, of HAuCl₄•3H₂O per 2VP unit and stirred for 24 h. HAuCl₄•3H₂O is not soluble in toluene but was incorporated into the star-block copolymer cores by coordinating with 2VP copolymer units. Upon coordination, the star-block copolymer solution in

toluene changes to light yellow in color. The inner P2VP chain can behave as a core in toluene, which is a solvent for PS but a nonsolvent for P2VP. Each of the 5 mL star-block copolymer solutions incorporated 0.1, 0.3 and 0.5 equiv of HAuCl_4 per 2VP unit and was added dropwise to 1, 3, and 5 mL of a 0.02 vol % solution of nonaqueous N_2H_4 in toluene, respectively. After reduction of HAuCl_4 for 12 h, the gold nanoparticles solution was diluted with dry toluene to 0.3 mg/mL on the basis of the star-block copolymer concentration.

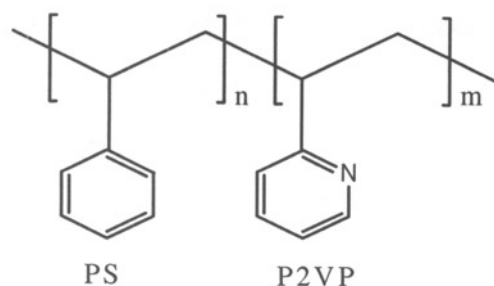
2 mM stock solutions of Cd^{2+} and S^{2-} ions were freshly prepared by dissolving 62 mg of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 100 ml of methanol and 48 mg of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 100 ml of methanol. A 2 mM solution of the capping agent 1-thioglycerol was also prepared in methanol. To prepare the CdS particles, a 0.5 ml aliquot of Cd^{2+} stock solution was added to the star-block copolymer solution, and the mixture was left for overnight stirring to ensure complete diffusion of the ions into the polar micelle core. Then, a 0.55 ml aliquot of the thioglycerol stock solution was added to the mixture, followed by addition of 0.3 ml aliquot of S^{2-} stock solution under constant stirring. All the reactions were done under a dry N_2 atmosphere. The ratio of the concentration of Cd^{2+} to S^{2-} ions during the synthesis was kept at 0.6. The resulting solution was colorless and glowed bright blue-green under UV illumination. The product did not show any evidence of precipitation for 3 months.

Results and Discussions

Star-Block Copolymer Synthesis

The synthesis of the star-block copolymer is shown in Figure 1.

1. Synthesis of PS-*b*-P2VP



2. Synthesis of Star Block Copolymer

PS-*b*-P2VP + Linking Agent
(EGDMA)

(Ethylene glycol dimethacrylate)
 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}-\text{OCH}_2\text{CH}_2\text{O}-\text{COC}(\text{CH}_3)=\text{CH}_2$

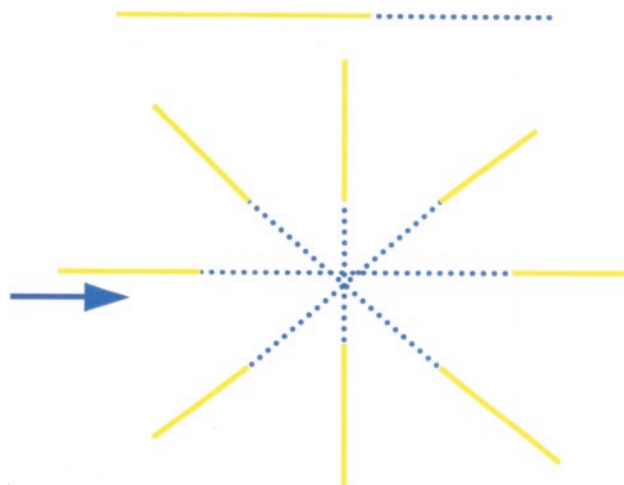


Figure 1: Synthesis of PS/P2VP Star-Block Copolymers

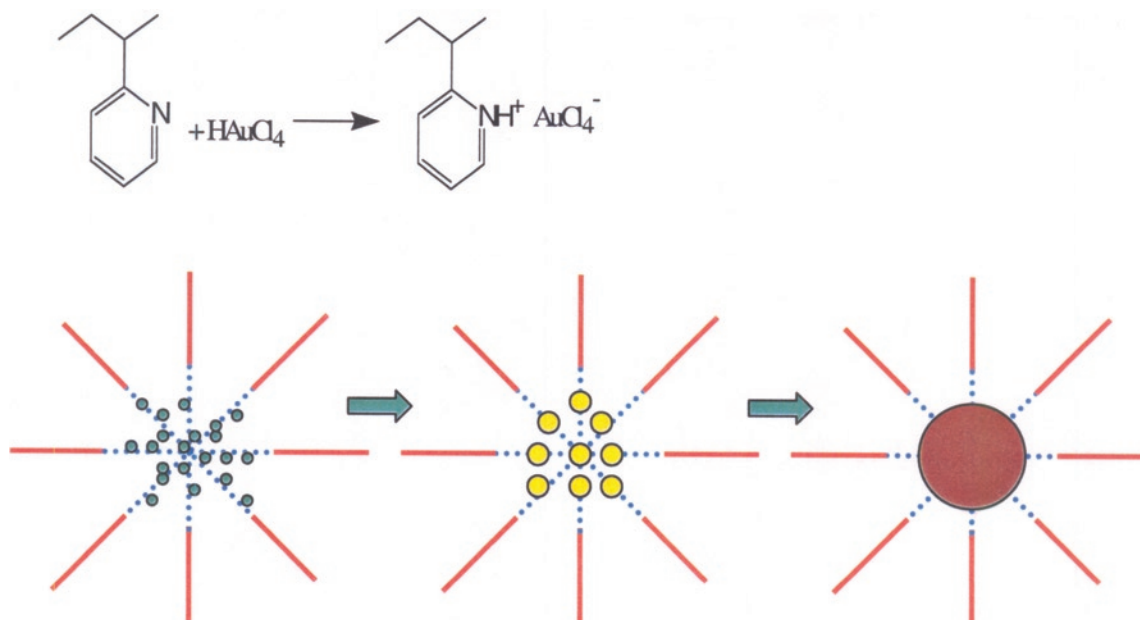
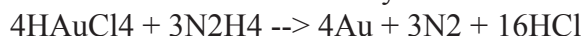
This strategy results in the ability to control the size and composition of the nanoreactor, since living anionic polymerization is used.

Gold Nanoparticle Synthesis

The synthesis of gold nanoparticles within the star-block copolymer nanoreactors is shown in Figure 2.

1. Interior block

2. Reduction with Hydrazine



“Seeded” star block copolymer

Reduction, Nucleation and Growth

Figure 2: Mechanism of gold nanoparticle growth.

Figure 3 shows the UV-vis absorption spectra of various gold nanoparticle solutions. After addition of a reducing agent, N_2H_4 , the yellowish colored solution of the star-block copolymer with incorporated HAuCl_4 changed immediately to a deep purple-red color. The absorption at 525 nm is assigned to the surface plasmon resonance of small gold nanoparticles.

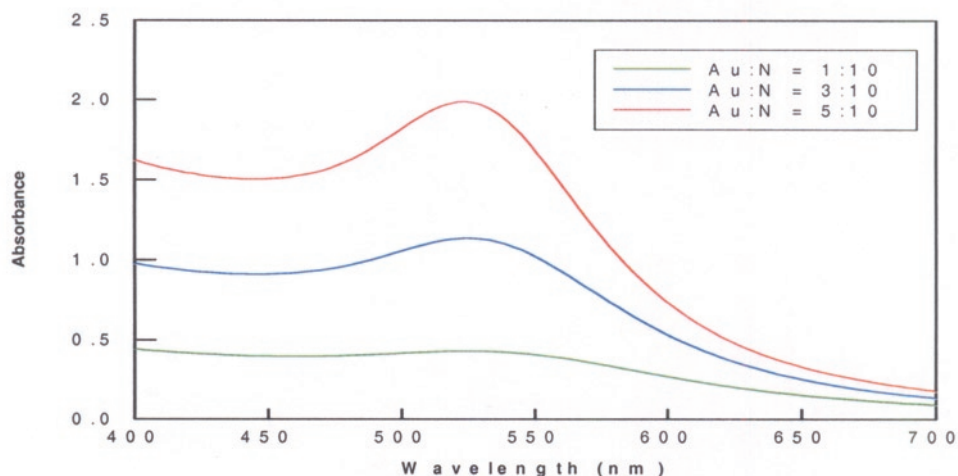
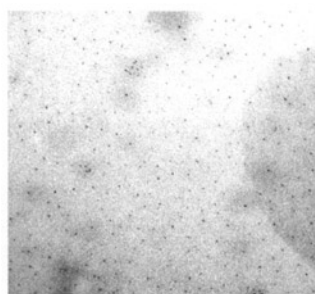


Figure 3: UV – Vis spectra of various gold nanoparticles.

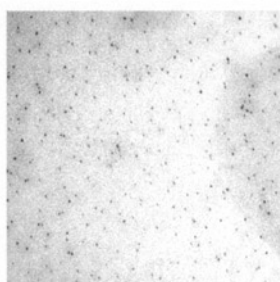
Key features of these spectra are:

- Absorption band at 525 nm for all samples: Surface plasmon resonance of Au nanocrystals)
- Increase of absorbance intensity with increasing the size of gold nanoparticles

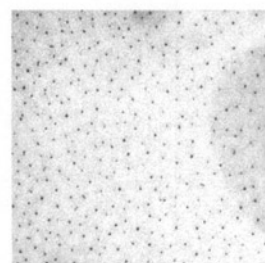
Figure 4 shows TEM Micrographs of gold nanoparticles for different incorporation ratios 24 hrs after reduction. It can be seen from the micrographs that gold nanoparticles of spherical shape and low polydispersity were formed. The average sizes of gold nanoparticles were 4.1, 5.5, and 6.7 nm for 0.1, 0.3, and 0.5 equiv of the incorporation ratio, respectively. It thus appears that 1 gold nanoparticle was formed in the core of a star-block copolymer for all incorporation ratios.



N:Au=10:1
Avg. Size: d=4.1 nm



N:Au=10:3
Avg. Size: d=5.5 nm



N:Au=10:5
Avg. Size: d=6.7 nm

Figure 4: TEM images of gold nanoparticles 24 hours after reduction.

Figure 5 shows TEM Micrographs of the gold nanoparticles shown in Figure 4 after aging for 1 month. In the case of 0.3 and 0.5 equiv samples, interestingly, larger gold nanoparticles than those observed 24 h after reduction were observed due to some aggregation and residual reduction, that is, resulting in a much broader size distribution of gold nanoparticles. Some of the gold nanoparticles were given larger than 5 times the initial average size due to the aggregation. However, in the case of the 0.1 equiv sample, the size distribution of gold nanoparticles remained the size distribution of gold nanoparticles remained unchanged for 1 month.

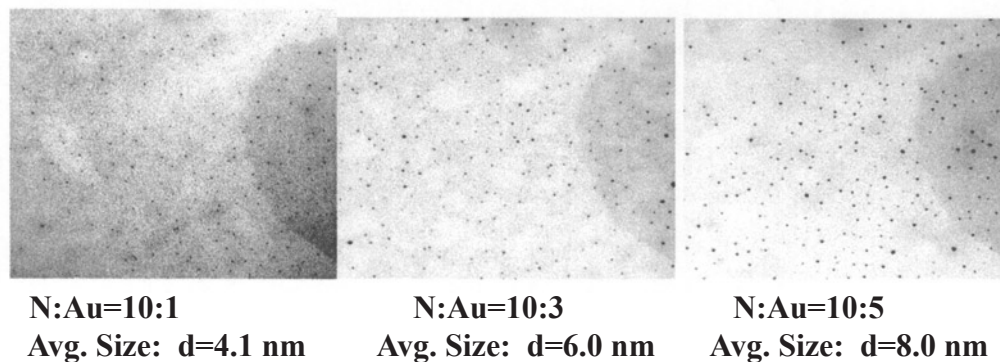


Figure 5: TEM micrographs of the gold nanoparticles of Fig. 4 after aging for 1 month.

CdS Nanoparticles

For comparison sake, CdS nanoparticles were grown both both star-block copolymers and in micelles formed using PS-P2VP diblock copolymers that had not been linked together using EGDMA. Figure 6(a) shows the TEM image of CdS nanocrystallites within PS-P2VP diblock copolymer micelles. It shows an abundance of nearly spherical particles whose size distribution is given by the histogram shown in Figure 7. It suggests that these nanocrystallites have a mean particle size in the range of 5-10 nm. The size distribution of these particles indicates the presence of two populations, one in the region of 5 nm and other around 10 nm. The 5 nm size particles probably arise due to their formation outside the micelles, while the 10 nm sized particles are likely to be formed within the core of the micelles. Figure 6(b) shows the TEM image of CdS nanocrystallites synthesized within star-block copolymer micelles. It also shows spherical particles with a particle size in the range of 15 nm. The size distribution of CdS particles prepared within star-block copolymer micelles is much narrower than the one prepared within the diblock copolymer micelles. This could be attributed to the stability of these micelle-like structures. In this case, there is no more concern about the micelle instability with time and concentration because the core segments of the star-block copolymer are *covalently bound*.

Conclusions

Micelles made of block copolymers of PS and PVP facilitate the synthesis of a range of metal and semiconductor nanoparticles of controlled size and shape. However, coarsening of the particles over time is a problem. Star-block copolymers, which are in effect stable covalently linked unimolecular micelles, have been found to be superior nanoreactors for nanoparticle synthesis. Not only are nanoparticles of controlled size and spherical shape obtained, but the nanoparticles are stable for extended periods (> 1 month). Thus, star-block copolymers appear to offer great promise for the growth of semi-conductor and metallic nanoparticles.

Acknowledgment

Funding from the NASA Microgravity Materials Research Program (NAG8-1678) is gratefully acknowledged.

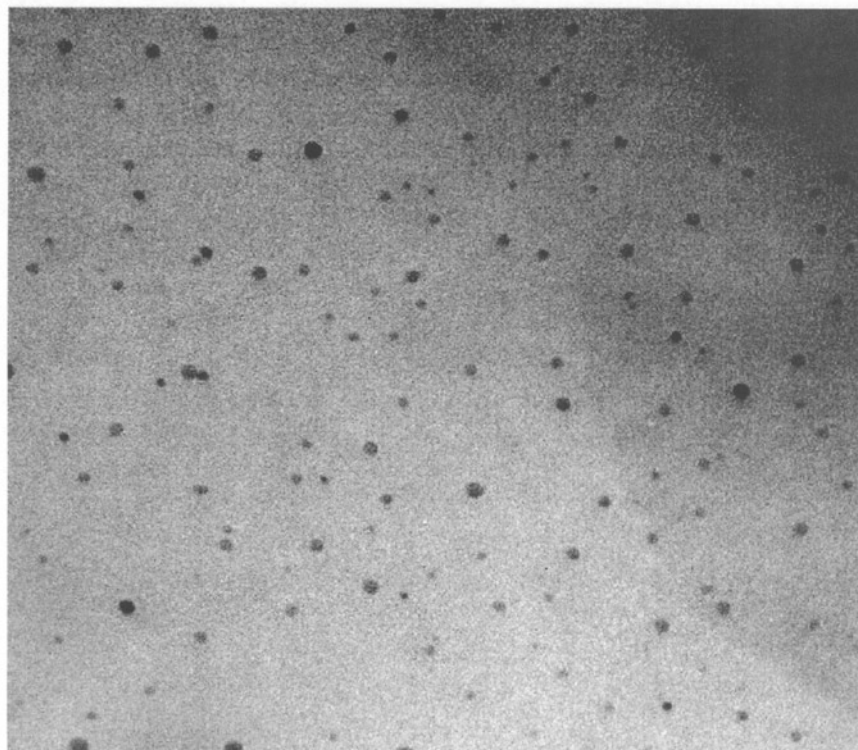


Figure 6a

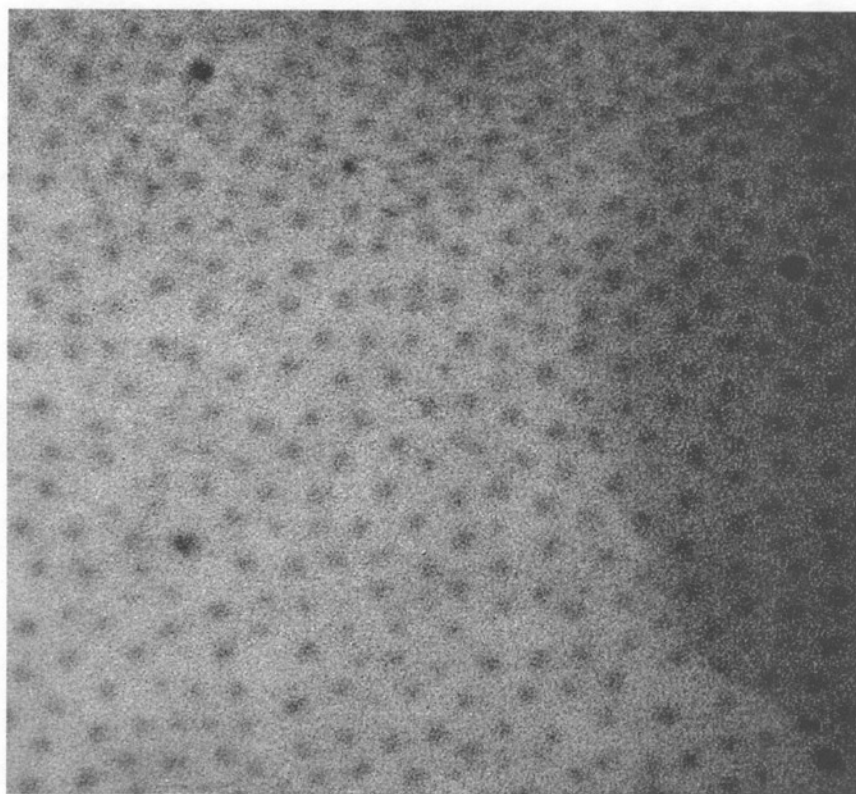


Figure 6b

Fig 6: TEM image of CdS nanocrystallites within PS-P2VP diblock (top) and star-block (bottom) Copolymer micelles.

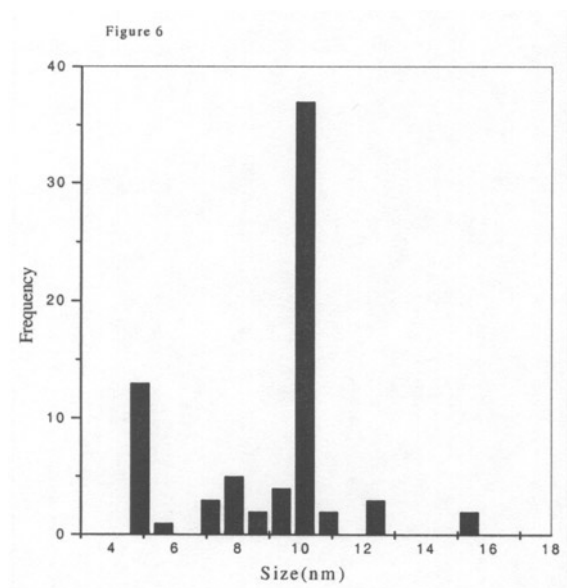


Figure 7: Particle size distribution of CdS Nanoparticles.

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CONTROL OF MELT CONVECTION USING TRAVELING MAGNETIC FIELDS

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Abstract

Applying an axisymmetric traveling magnetic field induces an axial Lorentz body force in the molten, cylindrical zone, during semiconductor crystal growth. This force can be conveniently controlled, in magnitude and in direction, and can benefit crystal growth applications. In particular, it can significantly offset the buoyancy force, which is often responsible for deleterious effects. Basics of this novel technological method as well as new results on the transition to time dependent flow are presented.

Traveling Magnetic Fields Technique

The crystal growth process is sustained by externally imposed thermal and solutal gradients. On earth, these gradients induce buoyancy convection in the melt that is often responsible for introducing undesired inhomogeneities at the growth interface. The proposed technique to counteract buoyancy, at least in the vicinity of the growth interface, may prove to be a valuable tool for understanding the relationship between convection and the introduction of defects into the crystal. It can also be valuable for industrial applications once the technique is fully understood and mastered. Static magnetic fields can be used for

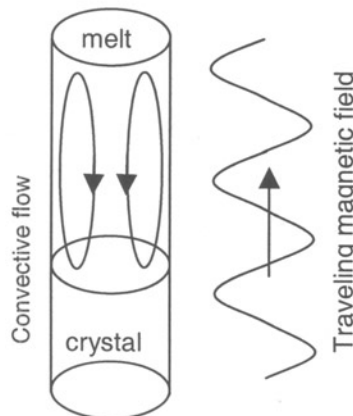


Fig.1. Schematic of TMF for VB configuration

this purpose but have limitations. A rotating magnetic field (RMF) is an example of a variable in time magnetic field and induces a primary swirling flow. A secondary meridional flow that develops due to this swirl could counteract the buoyancy. However, the body force induced by RMF is perpendicular to the buoyancy force in the melt, thus the magnitude of the total force increases. Conversely, a traveling magnetic field (TMF) is a direct way to induce a body force in the direction of gravity. Here one can adjust

Keywords: convection, control of convection, magnetic field, magnetohydrodynamics, new research

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the magnitude of the force by adjusting the strength of the magnetic field, not only to counteract the effects of buoyancy but also to create conditions similar to varying levels of gravity. In this approach a number of coils are placed co-axially around the charge. The coils, carrying out-of-phase harmonic currents, induce a meridional (axial and radial) Lorentz force in the electrically conducting melt. The geometry of the coils, the phase differences between them, the currents, and the modulation frequency can be used to control the magnitude and to some extent the distribution of the force field in the melt. The typical geometry of the proposed method is depicted in Fig. 1, a Vertical Bridgman (VB) configuration commonly used in research laboratories. For the uniform distribution of the electric current coils along the axis, an induced magnetic field can be approximated by a harmonic wave that can be represented by the vector potential in the form:

$$A = e_{\varphi} A_0 I_1(ar) \sin(\omega t - az)$$

This applied magnetic field induces a Lorentz force in electrically conducting medium, with the following time independent term:

$$\left\langle \frac{1}{\rho} \mathbf{j} \times \mathbf{B} \right\rangle = -\mathbf{e}_r \frac{\sigma a^2}{2\rho} v_r A_0^2 I_0^2(ar) - \mathbf{e}_z \frac{\sigma a^2}{2\rho} \left(v_z - \frac{w}{a} \right) A_0^2 I_1^2(ar)$$

where a is the inverse spacing between the coils, σ is the electrical conductivity, ρ is the density, A_0 is the amplitude of the applied vector potential, and the rest of the variables have their usual meaning (for more details, see¹).

On earth, this body force has to be added to the gravity induced force. The key idea is to minimize this resulting force. For long cylinders, commonly used in VB crystal growth, the buoyancy force is rather localized near the interface with the growing crystal. The uniform Lorentz force would not serve the purpose in such a case. Here we need a vertically localized force. This readily can be accomplished by selecting only a few coils with unequal currents and can reduce the buoyancy force significantly. We conducted modeling work on this topic and obtained a ten-fold reduction of the flow in the system for a non-optimized case. Although more accurate numerical minimization of the resulting force is possible, the experimental counterpart of this method could be difficult. We do believe, however, that the proposed technique gives sufficient flexibility for the crystal grower, as it allows one to set the flow pattern in an opposite direction as compared to only buoyancy driven flow. Moreover, if needed, the flow can be further reduced by applying a static plus traveling magnetic field combination. For a long cylindrical geometry, utilization of TMF is an ideal method for mixing or homogenizing electrically conducting melts as has been experimentally demonstrated².

At this point, fluid dynamics modeling of a TMF induced flow demonstrated a significant level of control of convective flow in the molten zone of a crystal growth ampoule. In particular, for short melt columns, such as used in float zone or traveling heater methods, a 40 times reduction of the global flow level can be achieved³. In the case of Vertical Bridgman, a 10-fold reduction can be obtained as previously indicated. Although a perfectly stagnant melt is not achievable, the convective roll direction can be changed. This is quite attractive for experimental investigations. Another direction of this research is focused on the flow stability. Here we need to know the steady flow boundaries and characteristics of the first bifurcation in the system. Our initial calculations indicate that the critical values for the magnetic Taylor number are in the area of 10^6 for an aspect ratio of 1, and 10^4 for the aspect ratio of 10, quite similar to RMF values. Fig. 2 illustrates the time evolution of the flow for a significant level of excitation, defined by the magnetic Taylor number, $T_m=10^6$. This numerical calculation is done for a diameter/height ratio of 1. The axisymmetric model is adopted and the flow is represented by the stream function. We observe here the oscillatory

flow with a non-dimensional period of 0.013. For smaller Taylor numbers, steady state laminar flow is established in the form of a single roll. Here, we see that the roll becomes unstable and splits into two rolls, which then recombine into one. For larger aspect ratios a set of several rolls emerges above some critical magnetic Taylor number, and the oscillatory behavior can be described by the pulsating of these rolls. The pattern resembles Taylor vortices, although the basic flow in our case is obviously not Couette flow.

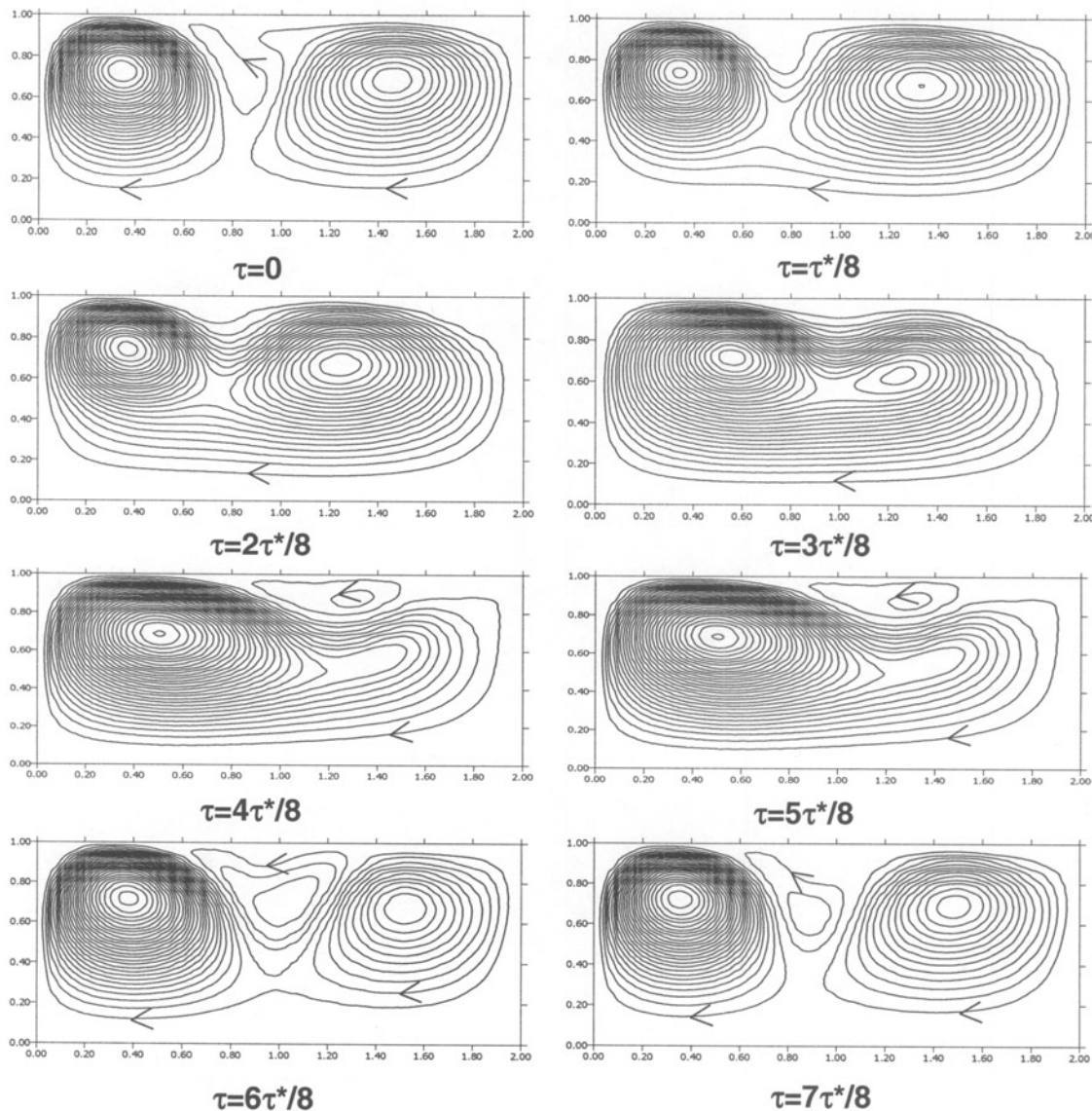


Fig.2. Stream function flow patterns for a single cycle. $Tm=10^6$.

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CONVECTIVE AND MORPHOLOGICAL INSTABILITIES DURING CRYSTAL GROWTH

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During crystal growth or solidification of a binary alloy from a liquid phase, temperature and solute gradients are inherently present and can give rise to fluid flow in the melt. The interaction of fluid flow with the crystal-melt interface^{1,2} plays an important role in determining the properties of the solidified material. Convection in the melt and interface instability may both produce solute inhomogeneities. The coupling between morphological instability and fluid flow can be complicated; interfacial instabilities depend on temperature and solute gradients that may be strongly influenced by the flow field. The flow field, in turn, may be influenced by the morphology of the interface.

A smooth crystal-fluid interface may become unstable during solidification, leading to cellular or dendritic growth. Linear morphological stability theory^{3,4} describes the conditions under which the interface becomes unstable. The original treatment of morphological stability by Mullins and Sekerka³ assumed local equilibrium at the crystal-melt interface and isotropy of the crystal-melt surface tension; this is an excellent approximation for many metals at low growth velocities. There have been many extensions of the theory in order to elucidate the role of external fields and additional physical effects on the stability demarcation.

We discuss recent research on temperature-dependent solute diffusivity and electrical effects during growth of a binary alloy from the melt and on anisotropic kinetics and shear flows during growth from a supersaturated solution. For these cases, we consider the stability of a planar interface during constant velocity growth V in the z -direction. The base state depends only on the z coordinate. The interface and the relevant fields (temperature, concentration, and flow velocity) are perturbed and are assumed to depend on time t and the lateral directions x and y as $\exp[i(k_x x + k_y y) + \sigma t]$, where k_x and k_y are wavenumbers in the x and y directions and the complex quantity $\sigma = \sigma_r + i \sigma_i$ governs the time-behavior of the system. The interface is unstable if $\sigma_r > 0$ for any values of the wavenumbers k_x and k_y . We also discuss the effect of a fluid flow due to density change upon monotectic solidification. The separation of scales during dendritic growth of a binary alloy due to the large ratio of thermal and solutal diffusivity is also presented.

Soret Diffusion and Temperature-Dependent Solute Diffusivity

The effect of a temperature-dependent diffusion coefficient on the morphological stability of a binary alloy during directional solidification has been determined⁵.

The solute flux J is assumed to have the form:

$$J = -D(T)\nabla C - [D_T(\xi_0 + \xi_1 C)]\nabla T \quad (1)$$

where $D(T)$ is the solute diffusion coefficient, which depends on temperature T , C is the solute

Keywords: morphological stability, temperature-dependent diffusivity, Peltier pulsing, anisotropic interface kinetics, shear flows, theoretical

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concentration, DT is the thermodiffusion coefficient (Soret effect), and ξ_0 and ξ_1 are constants. The case of a constant $D(T)$ with $\xi_1 = 0$ was first considered by Hurle⁶ and extended to the case $\xi_0 = 0$ and $\xi_1 = 1$ by Van Vaerenbergh *et al.*⁷ We focus on the temperature-dependence of the solute diffusion coefficient and neglect the Soret effect, i.e., $D_T = 0$. For tin-silver alloys, the diffusion coefficient varies linearly with temperature⁸.

For low velocities it is an excellent approximation to assume that the critical wavenumber at the onset of instability is much larger than the inverse diffusion length given by V/D_p , that is, $[k_x^2 + k_y^2]^{1/2} \gg V/D_p$, where D_p is the solute diffusion coefficient evaluated at the temperature of the planar interface. The resulting approximation to the dispersion relation with $\sigma = 0$ has the form

$$\Omega \left(1 - \frac{G_b}{mG_c} \right) - \frac{A\Omega^3}{k} - k + \left[\frac{k_s(G_s - G_L)}{2V(k_L + k_s)} \right] \frac{\partial D}{\partial T} = 0 \quad (2)$$

where $\Omega = [k_x^2 + k_y^2]^{1/2} D_p/V$, m is the liquidus slope, $G_b = (k_L G_L + k_S G_S)/(k_L + k_S)$, k is the segregation coefficient, $A = kT_M \Gamma V^2 / mG_c D_p^2$ is the absolute stability parameter of Mullins and Sekerka³ with $T_M \Gamma$ the capillary constant, G_c is the concentration gradient in the melt at the interface, G_L and G_S are the temperature gradients in the liquid and solid at the interface, and k_L and k_S are the thermal conductivities of melt and crystal. We note that $L_V V = k_S G_S - k_L G_L$ and $G_c = V(k-1)C_\infty / k D_p$, where L_V is the latent heat per unit volume and C_∞ is the bulk alloy concentration.

The interface is unstable when the left-hand-side of Eq. (2) is positive. At low velocities the first term in Eq. (2) is dominant and we obtain the modified constitutional supercooling criterion, i.e. the interface is stable if $G_b > m G_c$.

The left hand side of Eq. (2) has an extremum in Ω when

$$\frac{3A\Omega^2}{k} = 1 - \frac{G_b}{mG_c} \quad (3)$$

When this equation is combined with Eq. (2) we have

$$\Omega^3 = \frac{k}{2A} \left(k - \left[\frac{k_s(G_s - G_L)}{2V(k_L + k_s)} \right] \frac{\partial D}{\partial T} \right) \quad (4)$$

When the diffusion coefficient depends on temperature, the dimensionless wavenumber is modified to the extent that the second term in Eq. (4) is significant compared to the segregation coefficient.

Specific calculations were carried out for a tin-silver alloy.⁵ Although the temperature dependence of the diffusion coefficient has little effect on the critical concentration for the onset of instability, it causes a significant change in the wavelength at the onset of instability. For example, for $V = 0.5 \mu\text{m/s}$, the critical wavenumbers differ by a factor of two.

Electrical Effects

Electrical currents can modify the crystal growth process and affect morphological stability.^{9,10} An electrical current modifies the solute transport through electromigration, and the heat transport is modified by Joule heating and the Thomson effect. Here, we will focus on the change in the heat balance at the interface caused by the Peltier effect. Current pulsing is used to demarcate the solid-melt interface (see, e.g., Ref.

[11]). The solute segregation associated with current pulsing has recently been measured by Dabo *et al.*¹² in bismuth-antimony alloys for growth at a velocity of 4.17 $\mu\text{m/s}$ for pulses of 60 A/cm² with a duration of 0.5 to 10 s. The experimental results were compared with numerical calculations, which were based on a modification of an algorithm developed by Brush *et al.*¹³

In the presence of an electric current $I(t)$, the heat flux boundary condition at the crystal-melt interface is

$$VL_v + \Pi_{SL} I(t) = k_s \frac{\partial T_s}{\partial z} - k_L \frac{\partial T_L}{\partial z} \quad (5)$$

where T_s and T_L are the temperatures in the crystal and melt, and Π_{SL} is the Peltier coefficient. Basically, an electric current pulse modifies the interface velocity V , which in turn modifies the solute segregation.¹⁴ This solute segregation associated with a current pulse can be revealed by etching or by direct measurement of the concentration distribution. For a pure material with local equilibrium at the interface, the change in interface velocity ΔV associated with a sudden change in electrical current ΔI is simply given by $\Delta V = -\Pi_{SL} \Delta I / L_v$, which follows from Eq. (5) by assuming that the temperature gradients at the interface are not immediately affected by the current pulse.

In order to understand the behavior when the current is first applied to a binary alloy, a perturbation analysis has been carried out for small current pulses allowing for interface kinetics.¹⁵ Such a treatment is closely related to a morphological stability analysis for zero wavenumber, i.e., the interface remains planar. The time-dependence is treated using Laplace transform techniques. Initially there is no current, and, at $t = 0$, a current I_0 is applied. The change in interface velocity, ΔV , is given by

$$\Delta V = -\frac{\Pi_{SL} I_0}{a_1} \left[1 - \exp(a_1^2 t / a_2^2) \text{erfc}(a_1 \sqrt{t} / a_2) \right] \quad (6)$$

where $a_1 = L_v + K_b m C_\infty (k-1)/k\sqrt{D}$, $a_2 = K_b/\mu$, $K_b = k_s/\sqrt{\kappa_s} + k_L/\sqrt{\kappa_L}$, κ_s and κ_L are the thermal diffusivities of crystal and melt, and μ is a kinetic coefficient linearized about the initial velocity. At $t = 0$, $\Delta V = 0$, and the magnitude of ΔV increases to $|\Pi_{SL} I_0 / a_1|$ with a time constant $(a_2/a_1)^2$, i.e., when $(a_2/a_1)^2 = 1$, ΔV has reached 57 % of its final value. For a pure material $a_1 = L_v$, and we recover the simple limiting result $\Delta V \rightarrow |\Pi_{SL} I_0 / L_v|$. As the interface approaches local equilibrium, $\mu \rightarrow \infty$ and $a_2 \rightarrow 0$ so that the time constant approaches zero, i.e., the jump is instantaneous. Since the second term in the equation for a_1 is always positive, the magnitude of the jump is reduced to $|\Pi_{SL} I_0 / a_1|$ for an alloy. For the bismuth-1 wt % antimony alloy used in the experiments, a_1 is about two times larger than L_v and the time constant is 0.04 s.

Growth from a Supersaturated Solution

Growth from supersaturated solution usually exhibits facets indicating strong anisotropy and deviations from local equilibrium. For melt growth, many materials, including semiconductors and metals such as gallium and bismuth, also grow with facets. Experiments and theory indicate that a solution flowing above a vicinal face of a crystal can either enhance or prevent the development of step bunches.¹⁶⁻¹⁹ For growth on a prism face of ammonium dihydrogen phosphate (ADP), experiments by Chernov *et al.*¹⁷ showed that macrosteps develop on the portion of the growth hillock where the flow was down the hillock (in the direction of step motion). On reversing the direction of flow, the original macrosteps disappeared, but new macrosteps developed on the other side of the growth hillock. This indicated that flow in the direction of step motion is destabilizing and that flow opposite to the direction of step motion is stabilizing.

The motion of elementary steps is the essence of layerwise growth and decrystallization (dissolution, melting, or evaporation). Step motion does not always proceed as regular step trains; for regular step trains the interstep distance is constant and homogeneous crystals are produced. Under a wide range of conditions, the elementary steps cluster into step bunches; i.e., the interface is morphologically unstable with respect to step bunching. The step bunches trap impurities in amounts that depend on the local step densities, and therefore the impurity distribution differs from that formed by regular step trains. Step bunches themselves may, in turn, lose their stability and trap inclusions of solvent.

The effect of anisotropy of surface tension and interface kinetics on morphological stability has been treated²⁰ in a quasi-static approximation to the diffusion field; kinetic anisotropy causes traveling waves along the crystal-melt interface. Yuferev²¹ showed that for growth in which the interface is near a singular orientation (an atomically smooth orientation), there is an enhancement of morphological stability. In collaboration with Chernov, we have treated a number of topics related to growth from the melt or from supersaturated solution.²²⁻²⁸

In order to treat anisotropic kinetics phenomenologically, we assume that growth is by the motion of elementary steps, which leads to a macroscopic anisotropic kinetic law. The interface kinetic coefficient $\beta(p, s_0)$ is defined by the interface boundary condition

$$D\nabla C \cdot \mathbf{n} = \beta(p, s_0)(C_I - C_e) \quad (7)$$

where C is the solute concentration, C_e is the equilibrium solution concentration at the interface, the supersaturation $s_0 = (C_I - C_0)/C_0$, C_0 is the equilibrium concentration at a planar interface, the step density $p = \tan \theta$, where θ measures the deviation of the slope of the interface from a singular orientation and the subscript I denotes evaluation at the interface. At the planar interface C_I is given by $[(VC_s/\beta) + C_0]/[V/\beta + 1]$, where C_s is the concentration in the crystal. The kinetic coefficient is written as $\beta(p, s_0) = \beta_1(p) \beta_2(s_0)$. We restrict ourselves to the usual situation in which $d\beta_1/dp$ and $d\beta_2/ds_0$ are non-negative. In the simplest model for kinetic anisotropy, we take $\beta(p, s_0) = \beta_{st} |p|$, where β_{st} is a constant.

If the planar interface is a singular interface ($p = 0$), its kinetic coefficient vanishes and in this model there is no growth. In reality, a singular interface becomes macroscopically or locally vicinal due to a screw dislocation or a two-dimensional nucleation mechanism, which generates steps. A locally finite value of p at any macroscopic area of the interface then results.

Our sign convention is such that positive p corresponds to step motion to the left (negative x direction). If we consider a small sinusoidal perturbation of a planar interface characterized by a constant positive value of $p = p_0$, then regions of the perturbed interface with positive slopes will have larger values of p and therefore larger kinetic coefficients and larger step densities. Thus for the same supersaturation, regions of the interface with positive slopes will grow faster than regions with negative slope; this leads to a translation of the sinusoidal perturbed interface in the direction of the step motion. This lateral translation of the sinusoidal interface perturbation can move a depression in the interface to a solute-enriched region of solution where it can grow faster and thus provide a stabilizing mechanism. Similarly, the lateral flow of liquid can affect the stability.

A linear stability analysis for growth at constant velocity V in the z -direction into a supersaturated solution has been carried out. The incompressible Navier-Stokes equations for the fluid velocity $\mathbf{u}$ and the convection-diffusion equation for solute concentration $C(x, z, t)$ in the absence of gravity are solved.

A two-dimensional problem is considered so that all quantities are independent of the coordinate y . The density of crystal and melt are assumed equal.

The fluid velocity in the solution is measured in the laboratory frame in which the crystal is at rest, so that in the undisturbed state $\mathbf{u} = (U(z,t), 0, 0)$, where $U(z,t)$ represents the imposed shear flow velocity profile. We have considered shear flows of the simple form $U(z,t) = S z$, where S is the shear rate.

Under many conditions it is a good approximation to neglect the perturbed flow field¹⁸ and then the perturbed solute field can be obtained analytically in terms of Airy functions. For large wavenumbers, the Airy function can be simplified by using its asymptotic representation, and we can obtain a simplified stability criterion, namely

$$\left\{ \frac{\sigma_i}{k_x} \right\} \left\{ \frac{\sigma_i}{k_x} + \frac{S}{2k_x} \right\} > 2Dk_x V \left\{ 1 - \frac{C_0 \Gamma D k_x^2}{(C_s - C_0)(1 + B_c)V} \right\} \quad (8)$$

with

$$\sigma_i = \frac{VDk_x^2 (\partial \beta / \partial p)}{\beta^2 [1 + B_c + (Dk_x / \beta)]} \quad (9)$$

where Γ is the capillary length, and $B_c = (s_0/\beta)(\partial \beta / \partial s_0)$.

These formulas assume that $V/(2 D k_x) \ll 1$, $|\sigma|/(D k_x^2) \ll 1$, $|S|/(D k_x^2) \ll 1$, and $V/\beta \ll 1$; comparison of these formulas with numerical calculations indicate that they are good approximations except for small values of k_x .

Anisotropic kinetics results in a non-zero positive value of σ_i , which increases the left-hand-side of Eq. (8), and is stabilizing. The wavespeed σ_i / k_x is independent of the shear rate S and it is also clear from Eq. (8) that positive shear ($S > 0$), in which the flow is opposite to the direction of step motion, is stabilizing and that negative shear is destabilizing. In fact, for sufficiently large positive shear the system may be completely stable.²⁶

When B_c is positive, the capillary term in Eq. (8) is decreased, but this is important only for very large wavenumbers. For other wavenumbers, the main effect of B_c is to reduce σ_i , and hence to decrease the left-hand-side of Eq. (8); thus a positive value of $(\partial \beta / \partial s_0)$ is destabilizing. Experimental measurements on the (100) face of ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) have shown that the kinetic coefficient is a strongly nonlinear function of supersaturation^{29,30} and that the non-linearity may cause step bunching³⁰. If the kinetic coefficient increases with supersaturation, then a protuberance on the interface sees a higher supersaturation and will grow faster than a depression, which sees a lower supersaturation, and hence there is enhanced instability.

The behavior of the stability-instability demarcation ($\sigma_r = 0$) is shown in Fig. 1, where we plot the wavenumber as a function of the growth velocity.²⁷ For this plot we have taken $\beta = \beta_{st} p$, and used the following values for the parameters: $D = 5.0 \times 10^{-6} \text{ cm}^2/\text{s}$, $C_s/C_0 = 5$, $\Gamma = 5.0 \times 10^{-8} \text{ cm}$, $\beta_{st} = 4.0 \times 10^{-3} \text{ cm/s}$, $B_c = 0$, and $S = 0$. The solid curve in Fig. 1 corresponds to $p_0 = 0.005$. The interface is unstable for small velocities and intermediate wavenumbers. For small values of V there are two values of k_x , and as V increases the roots merge at a turning point. A simple formula for the turning point is given by

$$1 + B_c = \frac{27\Gamma V C_0}{16D(C_s - C_0)} \left[\frac{\partial \beta / \partial p}{\beta} \right]^4 \quad (10)$$

From Eq. (10), we have $V = (16/27) D (C_s - C_0) / (C_0 \Gamma p_0^4) = 1.48 \times 10^{-7}$ cm/s as the growth velocity below which there are at least two roots for k_x , namely the maximum velocity for instability. This value agrees well with the numerical value of 1.51×10^{-7} cm/s in Fig. 1.

When the step source for growth is a dislocation source that gives rise to a vicinal hillock, the vicinal face slope p_0 depends on the growth velocity or equivalently the supersaturation s_0 . The dashed curve in Fig. 1 is calculated for the same linear kinetic law but the slope is a linear function of supersaturation, $p_0 = p_1 s_0$, with $p_1 = 0.117$. The interface is unstable for large velocities and intermediate wavenumbers. The turning point can again be estimated from Eq. (10), but now we have $p_0^2 \approx (C_s - C_0) p_1 V / (C_0 \beta_{st})$. We then have no roots when $V < (16/27) (D/\Gamma) [(C_s/C_0) - 1]^3 (p_1/\beta_{st})^2 = 3.08 \times 10^{-7}$ cm/s, which is in good agreement with the numerical value of 3.15×10^{-7} cm/s.

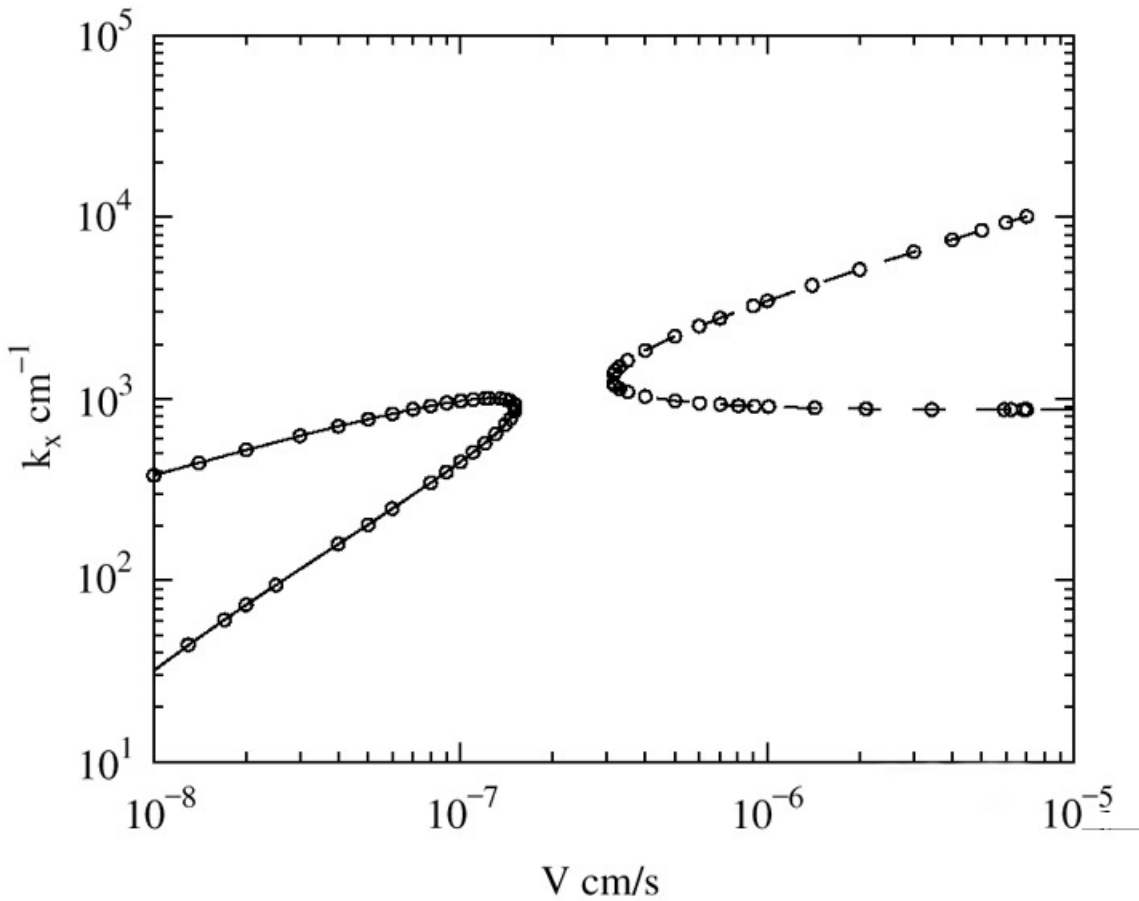


Fig.1. The spatial wavenumbers at which the system is neutrally stable as a function of growth velocity for linear kinetics ($\beta = \beta_{st} p$) with either a constant step density, $p_0 = 0.005$ (solid curve), or a supersaturation-dependent step density, $p_0 = 0.117 s_0$ (dashed curve). The curves are exact numerical computations, while the points are based on the approximate relation given by Eq. (8). The system is unstable inside the curves.

In the experiments of Chernov *et al.*¹⁷ the flow was periodically reversed. In order to study this situation we have considered²⁸ a flow in which the shear rate at the interface has the form $S = S_0 + S_1 \cos(\omega t)$, where S_0 and S_1 are constants. The stability analysis is based on Floquet theory in which instability corresponds to growth of the perturbation amplitude over a cycle. For a pure oscillatory flow $S_0 = 0$, the shear is stabilizing over half a cycle and destabilizing over the other half cycle. For large values of temporal frequency ω , the system can not respond to the oscillation and the results are the same as for steady shear. The results²⁹ are most sensitive to the oscillation frequency when $\omega \approx 1 \text{ s}^{-1}$. In the presence of a steady shear flow, modulation can either stabilize or destabilize the system, depending on the modulation amplitude and frequency. Numerical solutions of the linearized Navier-Stokes and diffusion equations and an approximate analytical treatment show that the flow oscillations weaken both the stabilization and destabilization induced by steady state flow. This weakening comes from mixing of solution above the perturbed interface and a modification to the phase shift between the interface perturbation wave and the corresponding concentration and flow waves. Optimal values of modulation frequency and amplitude are found when the steady flow is destabilizing.

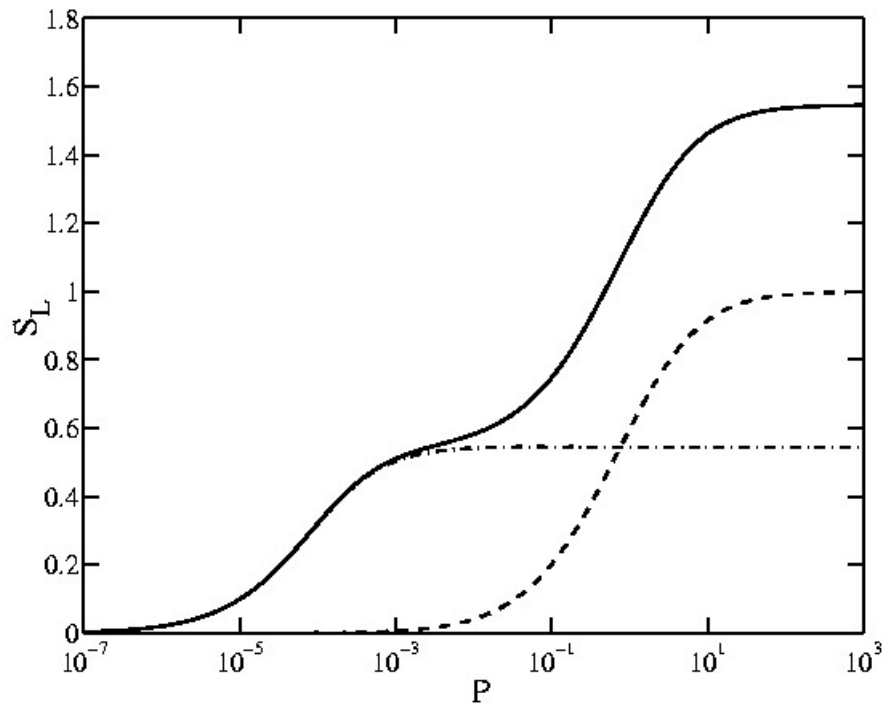


Fig. 2. Dimensionless supercooling S_L relative to the liquidus temperature according to Eq. (11) as a function of the thermal Peclet number P . The dashed curve is $I(P)$, and the dot-dashed curve is the second term in Eq. (11). The computation corresponds to an alloy of Al-0.15 mass fraction Cu, with $D = 2.1 \times 10^{-5} \text{ cm}^2/\text{s}$, $\kappa = 0.66 \text{ cm}^2/\text{s}$, $L_V/c_V = 374.0 \text{ K}$, $m = -0.08 \text{ K/mass fraction}$, and $k = 0.37$. In this case, $P_c = 3.1 \times 10^4 P$ and there is an obvious separation of scales of thermal and solutal effects.

Separation of Scales for Growth of an Alloy Needle Crystal

In collaboration with R.F. Sekerka,³¹ we have recently reexamined the problem of a needle crystal (model for a dendrite primary stalk) having the shape of a paraboloid of revolution growing at constant velocity V from a supercooled binary alloy of bulk concentration c_∞ and far-field temperature T_∞ . The coupled problem of thermal and solutal diffusion has been studied by a number of authors, and has been discussed

by Glicksman and Marsh.³² With solute present, the relation between undercooling and growth velocity is given by

$$I(P) + \frac{[m(k-1)c_{\infty}I(P_c)]/[L_v/c_v]}{[1-(1-k)I(P_c)]} = S_L \quad (11)$$

where $I(P)$ is the Ivantsov function,³¹ m is the liquidus slope, k is the distribution coefficient, c_v is the heat capacity per unit volume, and $S_L = (T_M + m c_{\infty} - T_{\infty})/[L_v/c_v]$ is the dimensionless supercooling relative to the liquidus temperature. Here $P = V\rho/2\kappa$ and $P_c = V\rho/2D$ are the thermal and solutal Peclet numbers, respectively. The form of Eq. (11) can be understood as follows: the function $I(P)$, which would be the only contribution to the supercooling for growth from a pure melt, has a sigmoidal shape and rises from zero to one, as shown by the lower dashed curve in Fig. 2. The second term in Eq. (11) also has a sigmoidal shape (as shown by the dashed-dot curve), and rises from zero to the asymptotic value $m c_{\infty} [(k-1)/k]/[L_v/c_v]$. The result of adding these terms can be understood very simply by taking advantage of the separation of scales of the thermal and solutal Peclet numbers. Indeed, the factor $\kappa/D \gg 1$, typically of magnitude 10^3 to 10^4 . Therefore the second term in Eq. (11) saturates while $I(P)$ is still relatively small compared to its saturation value. Hence the resulting curve has a nearly flat intermediate region where the two sigmoids join. To the left of this nearly flat region, the dendrites are “solutal” with $I(P) \approx 0$, whereas to the right of this region they are “thermal” with $I(P_c) \approx 1$. We note that $I(P_c) \approx 92\%$ of its saturation value for $P_c = 10$, so this crossover to the “thermal” region occurs for $P \approx 10 D/\kappa$.

Effect of Flow due to Density Change on Eutectic Growth

The Jackson-Hunt model³³ of eutectic growth has recently been extended³⁴ to allow for different densities of the phases. The density differences give rise to fluid flow, which is calculated from a series solution of the fluid flow equations in the Stokes flow approximation. The solute diffusion equation with flow terms is then solved numerically using an adaptive refinement and multigrid algorithm. The interface undercoolings and volume fractions are calculated as a function of spacing for tin-lead and iron-carbon eutectic alloys and for an aluminum-indium monotectic alloy. The numerical results are compared with various approximations based on the Jackson-Hunt analysis. The modified Jackson-Hunt analysis, which accounts approximately for the density differences, is in reasonable agreement with the numerical calculations: both the minimum undercooling and the lamellar spacing at the minimum undercooling agree to within less than 10 per cent. The modified Jackson-Hunt analysis is an approximation to the model used in the full numerical treatment in which lateral transport due to fluid flow is neglected. One might expect in general that the effective diffusivity of the melt increases if flow is taken into account, which should reduce the minimum undercooling and increase the lamellar spacing at the minimum undercooling. Comparison of the numerical results with the modified Jackson-Hunt analysis indicates that this occurs for the tin-lead and the aluminum-indium alloys, but the opposite actually occurs for the iron-carbon alloys. This argument, however, does not take into account the details of the relative contributions of convection and diffusion to the net lateral transport. The actual flow field that is induced by the density differences is in the opposite direction for iron-carbon compared to tin-lead and aluminum-indium. The qualitative effect of lateral convection is to enhance the lateral transport of solute for the tin-lead and aluminum-indium systems, and to diminish the lateral transport for the iron-carbon system.

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INVESTIGATION OF DYNAMIC OXYGEN ADSORPTION IN MOLTEN SOLDER JETTING TECHNOLOGY

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Abstract

Surface tension forces play a critical role in fluid dynamic phenomena that are important in materials processing. The surface tension of liquid metals has been shown to be very susceptible to small amounts of adsorbed oxygen. Consequently, the kinetics of oxygen adsorption can influence the capillary breakup of liquid-metal jets targeted for use in electronics assembly applications, where low-melting-point metals (such as tin-containing solders) are utilized as an attachment material for mounting of electronic components to substrates. By interpreting values of surface tension measured at various surface ages, adsorption and diffusion rates of oxygen on the surface of the melt can be estimated.

This research program investigates the adsorption kinetics of oxygen on the surface of an atomizing molten-metal jet. A novel oscillating capillary jet method has been developed for the measurement of dynamic surface tension of liquids, and in particular, metal melts which are susceptible to rapid surface degradation caused by oxygen adsorption. The experimental technique captures the evolution of jet swells and necks *continuously* along the jet propagation axis and is used in conjunction with an existing linear, axisymmetric, constant-property model to determine the variation of the instability growth rate, and, in turn, surface tension of the liquid as a function of surface age measured from the exit orifice. The conditions investigated so far focus on a time window of 2–4ms from the jet orifice. The surface properties of the eutectic 63%Sn-37%Pb solder alloy have been investigated in terms of their variation due to O₂ adsorption from a N₂ atmosphere containing controlled amounts of oxygen (from 8 ppm to 1000 ppm). The method performed well for situations where the oxygen adsorption was low in that time window. The value of surface tension for the 63Sn-37Pb solder in pure nitrogen was found to be 0.49 N/m, in good agreement with previously published work. A characteristic time of O(1ms) or less was determined for the molten-metal surface to be saturated by oxygen at 1000 ppm concentration in N₂.

Introduction

The modern electronics industry is developing a host of emerging technologies, which, when commercialized, are expected to reduce costs and dimensions of electronic devices, while simultaneously allowing a large throughput in electronic assembly. In the past fifteen years, as the integrated chip dimensions decreased, many new challenges have stemmed from the need to assemble these increasingly small components into fully functional entities. Solder Jet Technology or SJT [1] is one such application technique, which relies on inkjet printing principles to create and place monodispersed arrays of molten-solder droplets of approximately 50-100 μm diameter on a substrate containing the electronic circuit. The component is then put in contact with the array of “bumps” of solder deposited on the substrate board and,

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subsequently, the assembly is placed in an oven to remelt the solder and create, after solidification, solid conductive bonds between the parts.

Fluid interface phenomena involving droplet formation from a capillary jet are of central importance in SJT and surface tension is a crucial property affecting jet breakup. Due to the high reactivity of many liquid metals, the presence of surface active elements -even in low concentrations in the local atmosphere- degrades interface tension (σ) [2], which, in turn, compromises the effectiveness of the jetting process. Tin-containing melts are especially susceptible to surface degradation caused by oxygen adsorption [3]. Due to the ubiquitous presence of oxygen in the atmosphere, measurements of surface tension of metal melts exposed to O_2 are needed to assist the commercialization of SJT or other relevant technologies. It is important to note, however, that the time scales in jet capillary breakup are typically near or below a millisecond. This severe requirement disqualifies many standard methods of dynamic surface tension measurement, such as the sessile drop method used by Ricci et al. [4] to determine σ of molten tin over time scales ranging from 0.5 second to hours and in atmospheres with varying oxygen partial pressures. Using capillary jet instability techniques and low melting point metals, one can estimate the surface tension of newly formed surfaces within a time window of a few ms after formation, i.e., when surface properties have not been or are being compromised by adsorbed oxygen. In that sense, jet breakup methods appear to offer an advantage with respect to the temporal resolution afforded in liquid-metal systems, where the kinetics of oxygen adsorption can be quite fast. Although jet instability techniques have been used to determine interfacial tension of aqueous solutions in inkjet printing technology [5], these techniques have not been used to date for low melting point metals.

The experimental method presented herein offers clear advantages in terms of its simple non-iterative nature and its capability to define jet swells and necks at locations distributed *continuously* along the jet propagation axis. The experimental jet shape measurements are used in conjunction with an existing linear, axisymmetric, constant-property model to determine the variation of the instability growth rate, and, in turn, surface tension as a function of surface age measured from the exit orifice. The method is validated using pure water (constant surface tension), and an attempt is made to resolve the surface tension of eutectic 63%Sn-37%Pb solder (melting point of 183°C), as it varies due to O_2 adsorption from a nitrogen atmosphere containing controlled amounts of oxygen. The conditions investigated allow measurements within a time window of 2-4ms from the jet orifice, with temporal resolution down to a fraction of a millisecond. The limitations of the method are discussed, to provide guidance for future investigations in this area.

Theoretical Model

To describe the jet dynamics under the destabilizing action of surface tension, a linear model is adopted with the following assumptions:

- The jet flow is axisymmetric.
- Density ρ and viscosity μ of the liquid are constant over the entire jet length.
- Surface tension varies from one wavelength to the next, but remains constant within the same wavelength.
- The velocity profile is uniform over a cross section.
- Gravity is negligible.
- The drag forces exerted by the surrounding gas on the jet free surface are negligible.
- The disturbance is infinitesimal (i.e., linearity holds).

It is assumed that an infinitesimal radial perturbation, which grows exponentially is applied periodically. Therefore, the radial displacement δ of the jet surface is expected to be of the form

$$\delta(\eta, t) = \delta_0 e^{(\alpha + ik\eta)} \quad (1)$$

where α is the growth rate coefficient, $k = 2\pi / \lambda$, and η is the axial coordinate of a reference system moving with the jet velocity.

The previous hypotheses lead to the following dispersion relation [6]

$$\alpha^2 + \frac{2\mu k^2}{\rho I_0(kR_0)} \left[I_1'(kR_0) \frac{2kk^*}{k^2 + k^{*2}} \frac{I_1(kR_0)}{I_1(k^*R_0)} I_1'(k^*R_0) \right] \alpha - \frac{\sigma k}{\rho R_0^2} [1 - (kR_0)^2] \frac{I_1(kR_0)}{I_0(kR_0)} \frac{k^{*2} - k^2}{k^{*2} + k^2} = 0 \quad (2)$$

where the quantity k^* is defined by

$$k^{*2} = k^2 + \alpha \rho / \mu \quad (3)$$

and I_0 , I_1 are hyperbolic Bessel functions of the first kind of order 0 and 1, respectively. The primes in Eq. (2) indicate differentiation with respect to the argument of the function. As predicted by Eq. (2), the interval of instability (where $\alpha > 0$) is $0 \leq kR_0 \leq 1$. Equation (2) was used for the calculation of surface tension when all other parameters were known.

Experimental Apparatus

The apparatus could be operated at any liquid jet temperature between 20°C to 250°C, and included an environmental chamber consisting of an aluminum chamber of dimensions 22×22×25 cm fixed to a stainless steel breadboard.

The upper part of the chamber hosts the jetting device directed downward and mated to the bottom end of the supply reservoir containing the solder. This arrangement minimizes clogging of the device orifice, as most impurities float at the top of the reservoir with mostly clean metal forced through the capillary tube. The jetting device is fabricated by MicroFab Technologies Inc. and its primary component is a borosilicate glass capillary about 3 cm long manufactured by drawing and finely polished at the tapered tip. The orifice diameter is 150μm, which offers the right compromise between two competing requirements: the first, of a small diameter to enhance the effect of surface tension on instability, and the second, of a sufficiently large orifice to avoid capillary clogging by the impurities present in the molten metal alloy.

The jet velocity is controlled by the back pressure applied to the reservoir from the nitrogen tank. The nitrogen environment prevents oxidation at the surface of the liquid metal. From the second tank, a mixture of nitrogen and oxygen is directed into the chamber, while an oxygen analyzer monitors the concentration of the out-flowing gas mixture in real time.

The 63%Sn-37%Pb eutectic solder is heated by the resistors placed all around the reservoir. A real-time feedback control system consisting of the resistors, a thermocouple placed in contact with the solder cartridge and a temperature controller device enables to keep the temperature of the solder within $\pm 1^\circ\text{C}$ of the desired level during the experiment.

The harmonic voltage signal from a function generator is first amplified and then directed to the piezoelectric crystal surrounding the glass capillary, thus exciting the jet in a cyclical manner. The same signal triggers the LEDs placed behind the jet on the back side of the camera. The light source is strobed at the same frequency with the oscillating jet, so that the geometry of the jet surface can be observed clearly in a motionless state. This type of light source has been chosen particularly for the fast response to the voltage applied, yielding a strobe signal of narrow pulse, which is ideal for the current application.

Finally, an oscilloscope monitors the signal driving the piezoelectric crystal and displays the frequency and peak-to-peak voltage. The data from the experiment is produced from the jet images, which are collected using a CCD camera attached to a microscope lens. The typical spatial accuracy of the digitized images is $\pm 3\mu\text{m}$. Another camera, synchronized with the first one, is directed to the oscilloscope screen to record the frequency and voltage associated with each jet image.

Experimental Procedure and Data Analysis

The experimental procedure is a sequence of the following steps. First, the cartridge is filled with solder pellets and closed with a screw-on cap connected to the nitrogen tank. The chamber is closed and the tank valves are opened. Pure nitrogen flows through the cartridge interior, which contains the solder pellets, and reaches the chamber passing through the glass capillary; the controlled mixture of nitrogen and oxygen (if any) from the other tank flows directly to the chamber. When the oxygen concentration in the chamber stabilizes (in about 30 minutes), the heating elements are activated and the temperature of the cartridge gradually rises. When the liquid metal is at the desired temperature, the back pressure in the cartridge is raised and jetting starts. The disturbance introduced by the piezoelectric crystal excites the jet periodically. The velocity and frequency are set to their appropriate values and, finally, images of the jet are captured and stored. Subsequently, the images are processed to compute surface tension at specified spatial stations from the orifice.

Three major factors affect the jet shape, namely, ejection velocity, wavenumber and initial disturbance. The ejection velocity depends on the back pressure applied to the liquid pool. The wavenumber is set by the frequency of excitation of the piezoelectric crystal, while the amplitude of the initial disturbance is set by the applied voltage.

The first restriction imposed for the velocity range is the critical point represented by the partition line between varicose and sinuous breakup regime [7]. For velocities higher than the one corresponding to the critical point, the breakup regime changes from varicose to sinuous, and surface tension is no longer the major factor responsible for instability. In our case, the velocity is kept below that limit and the jet operates always in the varicose instability regime. On the other hand, the spatial growth of the instability is measured and a model for temporal growth rate is applied to determine the value of α . The error of this approach is of the order of β^{-2} [8], where β is defined by

$$\beta = (\rho R_0 / \sigma)^{1/2} U \quad (4)$$

In the above, U denotes the jet exit velocity, while R_0 is the jet exit radius. The β^{-2} accuracy implies that better agreement between spatial instability and temporal instability is expected for high-speed jets. In particular, it is required that $\beta \geq 3$. In the case of 63%Sn-37%Pb solder issuing through a $150\mu\text{m}$ orifice, this translates into velocities greater than about 2.4 m/s; in the reported experiments the velocity was kept in the range $3.5\text{m/s} \leq U \leq 6\text{m/s}$. These velocities, in conjunction with the limited capacity of the solder reservoir, resulted in each solder run lasting less than 2 minutes.

Equation (2) shows that surface tension is inter-related with five parameters, namely, viscosity μ , density ρ , wavelength λ (through the wavenumber kR_0), jet radius R_0 and growth rate α . While viscosity and density are taken from the literature, wavelength, jet radius and growth rate are measured experimentally. The associated errors in σ , due to errors in λ , R_0 and α , have been estimated using a standard sensitivity analysis and the known values for solder $\mu = 0.00195 \text{ Ns/m}^2$ and $\rho = 8218 \text{ kg/m}^3$.

In the present work, the growth rate is calculated by subtracting the radius (or diameter) of necks and swells measured at the *same* axial location. Figure 1 shows how this is achieved. This photo corresponds to an unstable water jet excited at a frequency corresponding to the maximum growth rate (i.e., minimum breakup length). The upper image (a) of the jet is taken without strobing; the image shows two contours. The outer one (separating black from grey) envelops the swells, while the inner one (separating grey from white) envelops the necks. This image shows the lengthwise progression of swells and necks along the jet. The other two images in Fig. 1 (b, c) are composites of (a) and frozen images of the jet outline taken in strobe mode at different phase angles between the function generator (driving the piezoelectric crystal) and the pulse generator (driving the illuminating LEDs). These two image overlays show how necks and swells exactly follow the envelopes identified in the top image. To calculate the growth rate α , we pick several points equally spaced along the axial coordinate (ten, for example), where the corresponding neck and swell diameter difference is calculated. The data obtained in this manner is fitted with an exponential curve ($e^{\alpha z/U}$), from which we determine the value of α applicable to this axial span. Typical axial spans, over which α is measured, extend to about 1.5λ , or in terms to time, to a fraction of a millisecond. These measurements are made at axial locations two to three wavelengths upstream of the drop detachment point, mainly to take advantage of the better definition of the jet outline there compared to locations closer to the orifice.

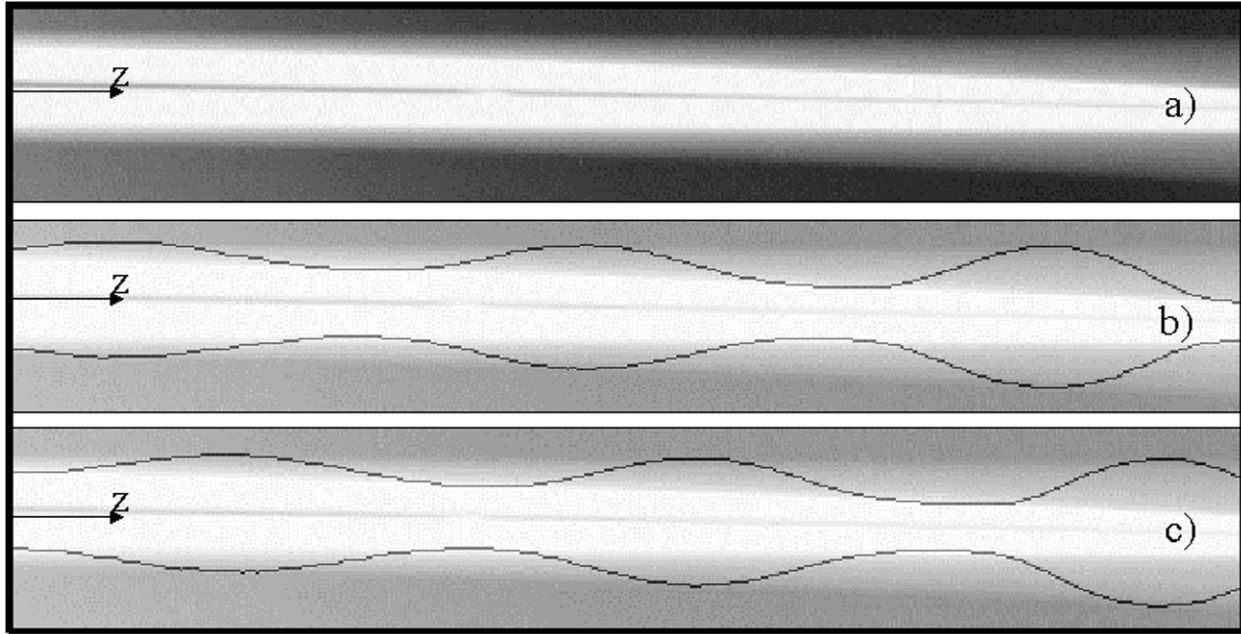


Fig. 1. Experimentally acquired images of an oscillating water jet for the growth rate calculation; a) overlay of many instantaneous images captured by the camera over a time period of 33ms, b) and c) instantaneous (frozen) images overlaid on (a). The slight downward tilt from left to right in all three images is a result of the inclined position of the camera.

The major advantage of this method, in comparison with the method used by Ronay [5], is that the measured value of α is based on a larger number of data stations along the jet length. This translates into a sensible reduction of the statistical scattering. An error analysis [9] showed that given the accuracy of the experimental instrumentation, the error in σ from the experimental uncertainty in determining the jet dimensions was rather high. The alternative way to measure α proposed herein allows not only a reduced error but also the identification of jet segments where the growth rate may no longer be exponential (near the breakup region, for instance).

Method Validation: Experiments with Water

To validate the experimental technique, tests were performed with deionized water, whose physical properties are known; at 20°C $\rho = 998.2 \text{ kg/m}^3$, $\mu = 1.002 \times 10^{-3} \text{ Ns/m}^2$, $\sigma = 7.28 \times 10^{-2} \text{ N/m}$. All water experiments were performed at a temperature of 20°C. As stated earlier, each measurement of α (likewise σ) was made over an axial span of $\sim 1.5\lambda$ located two to three wavelengths upstream of the drop detachment point. The average value of σ determined from six water experiments overestimated the actual value of surface tension by 3.8%, which is within the uncertainty, as calculated using standard procedures [9].

Experimental Results for 63Sn-37Pb Solder

The solder used in the experiments is a high-purity eutectic alloy of tin and lead (63%Sn-37%Pb) produced by Witmetaal. This low-melting point material (183°C) is used for electronic components, such as computers and communications equipment, where only moderate heat exposure can be tolerated by the delicate components. The material mass composition analysis, as provided by the manufacturer, is (%): Sn 63.41, Ni ≤ 0.001 , Sb 0.009, Bi 0.006, Cd ≤ 0.001 , Cu 0.001, Ag ≤ 0.001 , Zn ≤ 0.001 , Al ≤ 0.001 , Fe ≤ 0.001 , In 0.002, As ≤ 0.001 , Pb Balance.

Table 1 below lists the conditions for four experiments performed using solder. In all cases, the temperature of the molten metal was maintained at 240°C. For each case, additional information is provided in the table regarding the oxygen content in the nitrogen atmosphere, as well as the surface age at the point of measurement. Surface age is defined as the time period required for the jet to traverse from the orifice to the axial point where each measurement is made. As explained earlier, measurements are made over regions two to three wavelengths upstream of the drop detachment point. It is emphasized that α is measured over an axial span of $\sim 1.5\lambda$, which corresponds to a temporal span of about 0.3ms. So although the measured value of α (likewise σ) corresponds to a time window, the extent of this window (0.3ms) is low enough, such as to consider this measurement instantaneous compared to the longer period ($>2\text{ms}$) required for the fluid to reach the measurement station after exiting the orifice (where surface age = 0). The uncertainty in σ , as listed in the last column of Table 1, was estimated using standard methods [9]. It is apparent that the calculated values of σ for surface ages between 2-4ms are narrowly distributed around 0.49 N/m, which compares favorably with the range of 0.50-0.51 N/m reported in [10] for 60%Sn-40%Pb solder and temperatures between 210-250°C. Carroll and Warwick used a maximum bubble pressure technique to obtain these values. Hoar and Melford [11] used a capillary rise technique to obtain values from 0.535 N/m down to 0.520 N/m in the temperature range of 180 to 230°C for an alloy containing 61.6% Sn by weight. White [12] employed a sessile drop technique and obtained values of 0.480-0.485 N/m for a 60.12% Sn alloy in the temperature range of 220-260°C.

Table 1. 63Sn-37Pb solder data: Experimental parameters and results

O ₂ conc. [ppm]	Surface Age [ms]	Jet Dia. [μm]	Frequency [Hz]	Velocity [m/s]	Growth Rate (α)	Surf. Tension σ [N/m]
20	2.5	147	9135	5.96	4218	0.480±0.027
17	2.0	147	7265	5.13	4186	0.499±0.029
12	2.1	153	8375	4.85	3550	0.480±0.053
8	4.0	153	6000	3.41	3483	0.487±0.075

The surface tension values listed in Table 1 correspond to surface ages in the range 2-4ms. This range was possible by changing the jet exit velocity and using the same solder jetting device, which featured a 150μm-diameter orifice. In principle, surface ages lower than those listed in Table 1 can be attained by either conducting measurements closer to the orifice, or using a smaller diameter orifice. Unfortunately, the latter option was not possible due to the associated increased risk of clogging combined with the limited availability of solder jetting devices in the commercial market. Thus, an attempt was made to conduct measurements closer to the available orifice. It was found that the error in σ increased with distance from the optimum location, which is positioned 2-3 wavelengths upstream from the breakup point. Consequently, this increased error did not allow any definitive conclusions regarding the value of σ at surface ages below 2ms.

It is noted that the oxygen concentration in all four runs of Table 1 is quite low, essentially corresponding to jetting in a nearly pure nitrogen atmosphere. Additional solder experiments have been conducted using an ambient oxygen concentration of 500 ppm (0.05% in nitrogen), with the goal to resolve surface tension variation with surface age. The oxygen surrounding the molten metal jet is adsorbed to the surface, thus lowering the value of surface tension [3]. However, the values of σ obtained under these conditions were low and out of the reasonable range determined from thermodynamic considerations [10]. The unreasonably low values of σ may be due to the excessively simple theoretical model adopted, which is inadequate in those cases in which surface tension changes rapidly along the axial coordinate owing to the adsorption of oxygen from the surroundings. Here, a model that accounts for the coupling effect of both capillary instability and oxygen adsorption, for example, similar to the one proposed by Artemev and Kochetov [13], might give a better description of the dynamics of the disintegrating jet. An additional reason for the poor performance of the present model in cases where O₂ content is non-negligible could be non-uniform oxygen transport rates over swells -as compared to necks- which, in turn, cause variations of σ along a single wavelength. The present model does not consider variation of σ along a single wavelength. Nevertheless, with the present experimental technique, it would be possible to trace the evolution of necks and swells along the axial coordinate and, thus, potentially validate a more encompassing model that accounts for the above chemical or physical transport mechanisms. The identification of such theoretical model is out of the scope of the present effort.

The highest oxygen concentration used in the solder experiments was 1000 ppm (0.1% in nitrogen). Beyond this limit, the surface apparently saturated so quickly that the jet did not respond any longer to the excitation induced by the piezoelectric crystal, irrespectively of the applied frequency and voltage. A concentration of 1000 ppm appears to be the limiting value for controlling the breakup of molten 63Sn-37Pb solder by induced capillary instability under the conditions investigated herein. This result, in turn, suggests a characteristic time of O(1ms) or less required for the molten-metal surface to be saturated by oxygen at this concentration (1000ppm). The kinetic-fluidynamic diagrams for liquid metal-oxygen

systems reported in [14] allow the estimation of the time required to form an adsorbed oxygen monolayer on the melt surface exposed to an inert carrier flow containing definite amounts of oxygen. For molten tin at 232°C, this time was reported to be ~44s at 1ppm O₂ in Helium. If one assumes linearity, the oxygen monolayer formation period at 1000ppm would be 44ms for pure tin, a time period that substantially exceeds the one designated in the present work. This discrepancy may be due to the presence of nitrogen (instead of He) in the current work, or the presence of Pb in the molten multicomponent phase. It may also be attributed to the inherent differences between the two physical configurations, which affect the gas diffusion layer characteristics above the liquid metal surface, and, in turn, the transport of oxygen molecules to it.

Conclusions

An oscillating capillary jet method has been developed for the measurement of dynamic surface tension of liquids, and in particular, metal melts which can rapidly react with surface active elements (such as oxygen) in the ambient atmosphere. The technique captures the evolution of jet swells and necks *continuously* along the jet propagation axis and allows measurement of interfacial tension within a time window of a few milliseconds from the orifice.

The experimental technique was used in conjunction with an existing linear, axisymmetric, constant-property model to determine the variation of the instability growth rate, and, in turn, surface tension of the liquid as a function of surface age measured from the exit orifice. The conditions investigated featured measurements within a time window of 2-4ms from the jet orifice, with temporal resolution down to a fraction of a millisecond. In test experiments conducted with a pure substance (deionized water), the value of σ calculated was well within 5% of the known value. An attempt was made to resolve the surface tension of the eutectic 63%Sn-37%Pb solder alloy (melting point of 183°C), and its variation due to O₂ adsorption from a nitrogen atmosphere containing controlled amounts of oxygen (from 8 ppm to 1000 ppm). The combination of experiment and model performed well for situations where the oxygen adsorption was low in that time window. The values of surface tension for the 63Sn-37Pb solder in a virtually pure nitrogen ambient was found to be 0.49 N/m, a value that is in good agreement with other published studies. However, in cases where oxygen adsorption degraded the melt surface too rapidly, the theoretical model proved inadequate. Despite the shortcomings of the tested model, the experimental technique could be useful in validating a more encompassing model that accounts for the coupling effect of capillary instability and oxygen adsorption (in other words, allows for variation of interfacial tension within a single wavelength).

An oxygen concentration of 1000 ppm was found to be the limiting value for controlling the breakup of molten 63Sn-37Pb solder by induced capillary instability under the conditions investigated herein. This result, suggests a characteristic time of O(1ms) or less required for the molten-metal surface to be saturated by oxygen at this concentration.

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RADIATION TRANSPORT PROPERTIES OF POTENTIAL IN SITU-DEVELOPED REGOLITH-EPOXY MATERIALS FOR MARTIAN HABITATS

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Abstract

Mission crews in space outside the Earth's magnetic field will be exposed to high energy heavy charged particles in the galactic cosmic radiation (GCR). These highly ionizing particles will be a source of radiation risk to crews on extended missions to the Moon and Mars, and the biological effects of and countermeasures to the GCR have to be investigated as part of the planning of exploration-class missions. While it is impractical to shield spacecraft and planetary habitats against the entire GCR spectrum, biological and physical studies indicate that relatively modest amounts of shielding are effective at reducing the radiation dose. However, nuclear fragmentation in the shielding materials produces highly penetrating secondary particles, which complicates the problem: in some cases, some shielding is worse than none at all. Therefore the radiation transport properties of potential shielding materials need to be carefully investigated. One intriguing option for a Mars mission is the use of material from the Martian surface, in combination with chemicals carried from Earth and/or fabricated from elements found in the Martian atmosphere, to construct crew habitats. We have measured the transmission properties of epoxy-Martian regolith composites with respect to heavy charged particles characteristic of the GCR ions which bombard the Martian surface. The composites were prepared at NASA Langley Research Center using simulated Martian regolith, in the process also evaluating fabrication methods which could lead to technologies for *in situ* fabrication on Mars. Initial evaluation of the radiation shielding properties is made using radiation transport models developed at NASA-LaRC, and the results of these calculations are used to select the composites with the most favorable radiation transmission properties. These candidates are then evaluated at particle accelerators which produce beams of heavy charged particles representative in energy and charge of the radiation at the surface of Mars. The ultimate objective is to develop the models into a design tool for use by mission planners, flight surgeons and radiation health specialists.

Introduction

Possible adverse effects on astronaut health from extended exposure to the space radiation environment are a critical issue for the human exploration and development of space. Crews on long-duration missions outside the protective effects of the Earth's magnetic field will be exposed to relatively high numbers of high energy ions (HZE) in the galactic cosmic rays (GCR) (Fig. 1). These ions ($Z>1$), while small in number compared to the total GCR charged particle flux, can contribute substantially to radiation risk by virtue of their high energy deposition: a single particle traversal can kill, or what can be worse, severely damage a cell, which can lead to cancer (Fig. 2) [1]. Long term effects of GCR HZE particles have been identified by the National Research Council [2] as the principal radiation risk to astronauts on extended stays outside low Earth orbit.

Keywords: radiation protection, GCR, heavy ions, ISRU, Martian regolith

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Future astronauts will spend many months in habitats on the Martian surface. As a material for habitat construction, Martian regolith-epoxy composites offer favorable radiation transmission properties and structural advantages [3,4], and can potentially be fabricated using primarily *in situ* resources from the Martian soil and atmosphere, thus reducing the weight which will have to be carried on the Mars transit vehicle. These potential benefits must be considered in the context of a full mission scenario, including the challenges of transporting the necessary precursor chemicals and equipment to the Martian surface and safely processing the *in situ* resources into usable materials. It is therefore important to establish the radiation transport properties of candidate materials early on, so that if they are sufficiently promising, the necessary trade studies can be carried out. Model calculations and selected experiments at particle accelerators are being used to evaluate the radiation transmission properties of regolith-epoxy composites. The accelerator-based measurements produce detailed data on radiation transport properties of selected materials with respect to significant components of the GCR HZE. These data will be used both to quantify the radiation shielding effectiveness of the candidate materials and to improve the accuracy of the models. Ultimately the models, in combination with data from radiobiological experiments now in progress, will comprise a design tool for use by mission planners, flight surgeons and radiation health specialists.

Methods

The experimental setup is shown in Fig. 3. (For a more detailed description of the experimental methods, see Refs. [5,6]). All detectors were silicon solid state. Particle identification was by energy loss in the silicon. The detectors before the target were used to identify primary beam ions. The detectors after the target recorded charge and energy of surviving primary ions and produced fragments. The downstream detectors subtended small angles around the beam axis, and thus for most events recorded a single primary ion or a small number of fragments at or near the beam velocity. The fragment ΔE spectrum can be converted to a charge distribution by making use of the fact that when all particles are at or near the same velocity, the energy loss of charged particles in this energy range is approximately linear in Z^2 . Targets were fabricated at NASA-Langley Research Center by mixing polymer with simulated Martian regolith and de-aerating the mixed powder under vacuum at 71° - 77°C. Measurements are being carried out with heavy ions at the Brookhaven National Laboratory Alternating Gradient Synchrotron (BNL AGS) and the Heavy Ion Medical Accelerator at Chiba, National Institute of Radiological Sciences, Japan (NIRS HIMAC). Data have thus far been taken with the following ions/energies: 1087 MeV/u ^{56}Fe ; 600 MeV/u ^{28}Si ; 400 MeV/u ^{14}N ; 290 and 400 MeV/u ^{12}C .

Results and Discussion

Figures 4 and 5 show some representative results of the nuclear fragmentation measurements for 400 MeV/u carbon ions and 1087 MeV/u iron ions. (Iron is the heaviest ion present in significant numbers in the GCR.) These plots show numbers of recorded fragments as a function of energy deposited in a pair of 3 mm silicon detectors. The abscissa is number of ADC channels, which is readily converted to energy in MeV. Since energy loss is a function of fragment charge and velocity, and since most fragments near the beam axis are at roughly the same velocity, each peak represents a discrete charge state, a single charge in most cases, but some multi-fragment states, as well. These data illustrate the degree to which relatively modest amounts of shielding materials fragment high energy GCR nuclei. Measurements such as these are being used to quantify the effects of various materials and to benchmark and improve the models [7-10].

It is not sufficient, however, to make physical measurements: the biological effects of the entire produced particle spectrum must be taken into account. For example, the produced fragments, while less ionizing

and therefore lower dose, are also more penetrating. Systematic accelerator studies of effectiveness of regolith composites as a function of incident particle charge and energy, and material composition and thickness need to be coupled to transport model development and eventually to biological data and models of biological effects, in order to have a tool for selection of composites with the most promising combinations of structural and radiation shielding properties.

Summary and Conclusions

Model calculations and measurements at particle accelerators are being used to evaluate the radiation transmission properties of Martian regolith composites. The accelerator measurements produce detailed data on radiation transport properties of selected materials with respect to significant components of the GCR HZE. Several regolith composites fabricated at NASA-LaRC have been modeled using two different benchmarks of biological effectiveness and then exposed to HZE beams at the BNL AGS and NIRS HIMAC. Nuclear fragmentation spectra have been recorded for charged projectile fragments produced in the forward direction. These data will be used both to quantify the radiation shielding effectiveness of the candidate materials and to improve the accuracy of the models. Ultimately the models, in combination with data from radiobiological experiments now in progress, will comprise a design tool for use by mission planners, flight surgeons and radiation health specialists.

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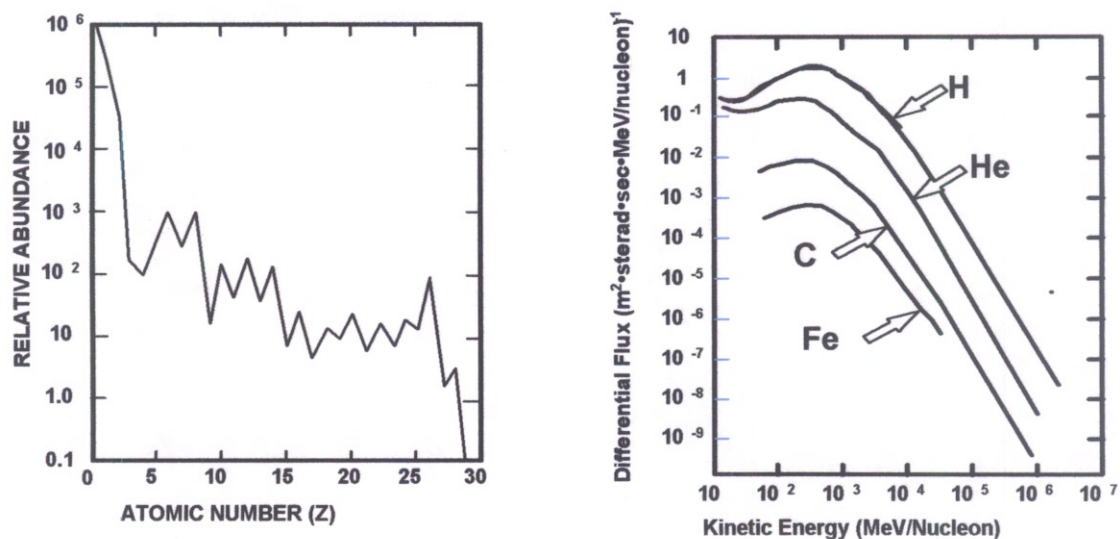


Figure 1. Distribution of GCR particles in atomic number, Z , and energy. The HZE particles relevant for space radiation risk range up to iron ($Z = 26$) and have energies up to several thousand MeV/nucleon.

Predicted Biological Responses Behind Various Materials After 1 Year GCR Exposure

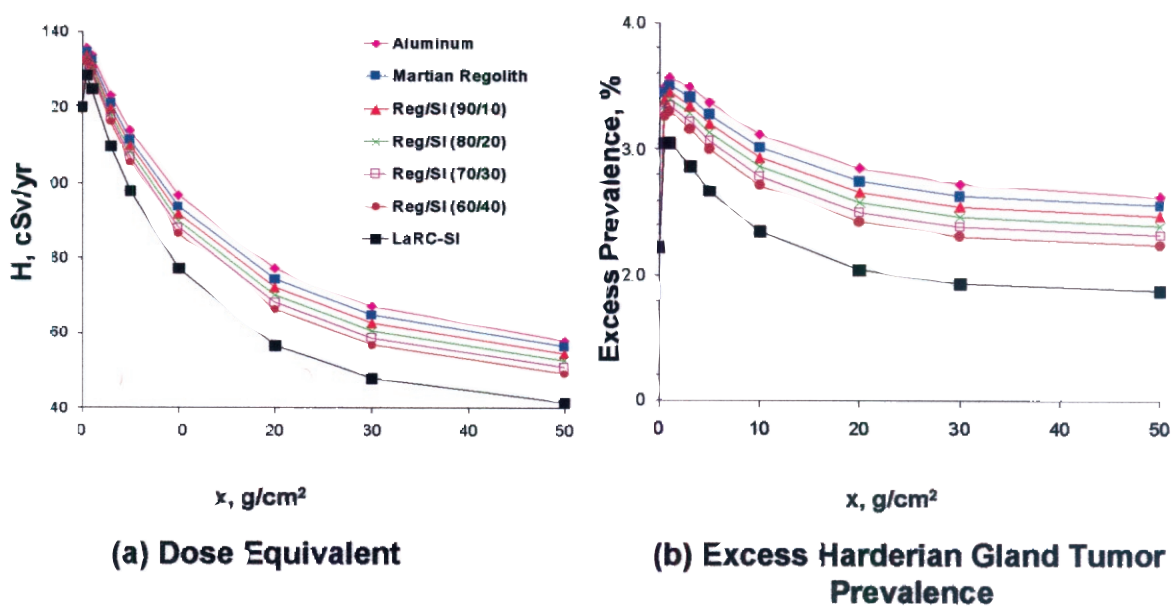


Figure 2. Calculated biological responses to space radiation, using two measures of biological effect: standard dose equivalent and excess tumor prevalence in the mouse Harderian gland.

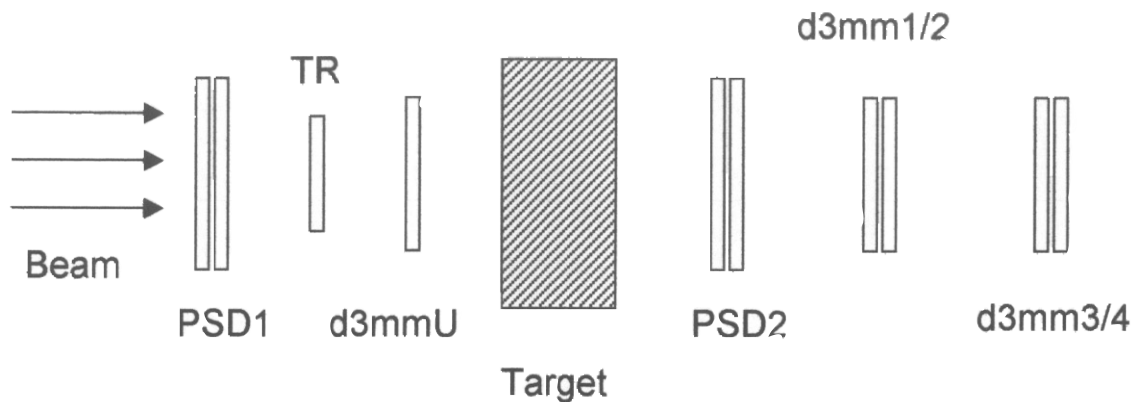


Figure 3. Typical detector setup. All detectors are lithium-drifted silicon. “PSD” denotes position-sensitive detectors.

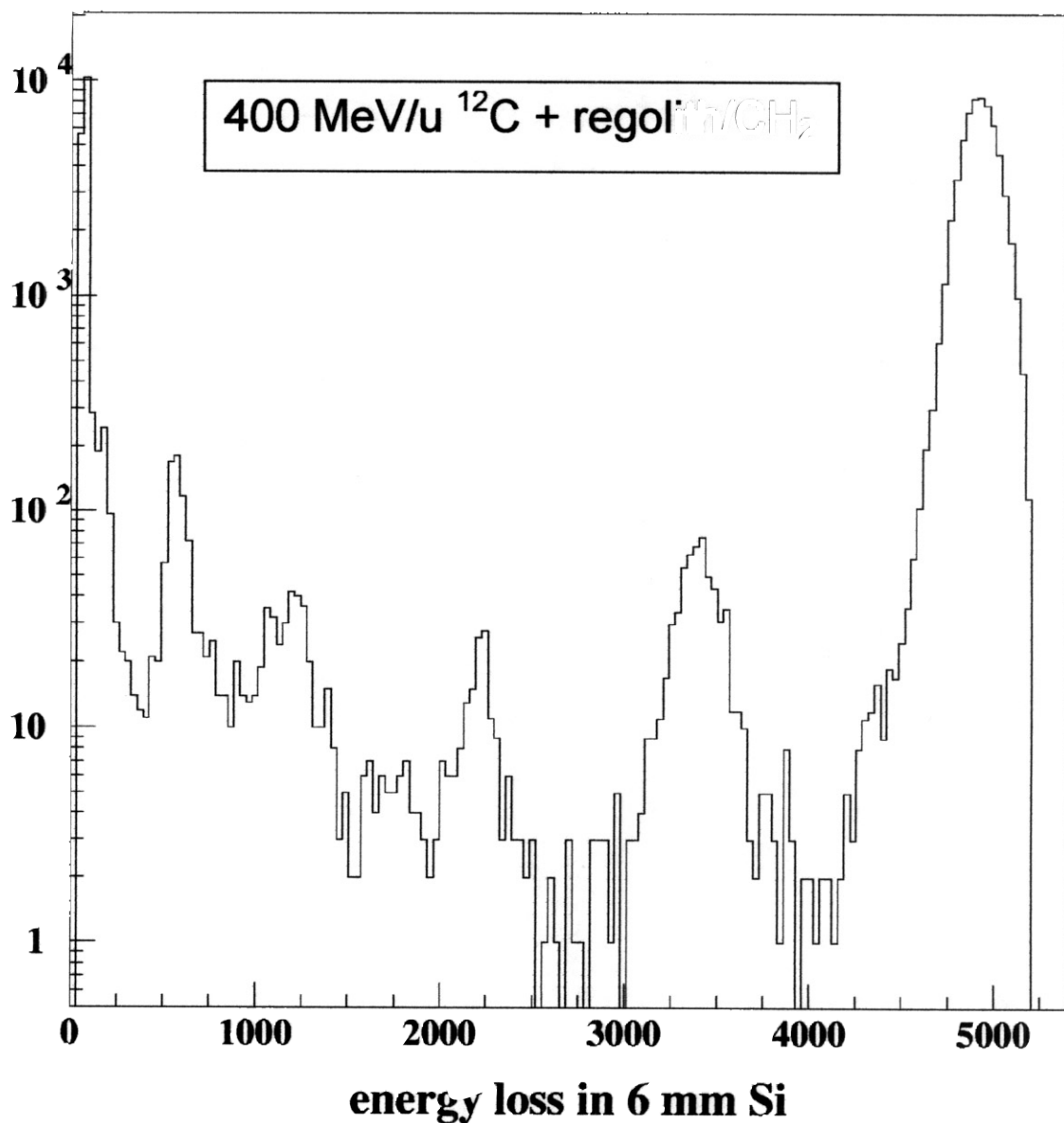


Figure 4. Number of fragments produced in 5 gm/ cm² Martian regolith composite (85% regolith / 15% CH₂) as a function of energy loss in by a 400 MeV/u ^{12}C beam.

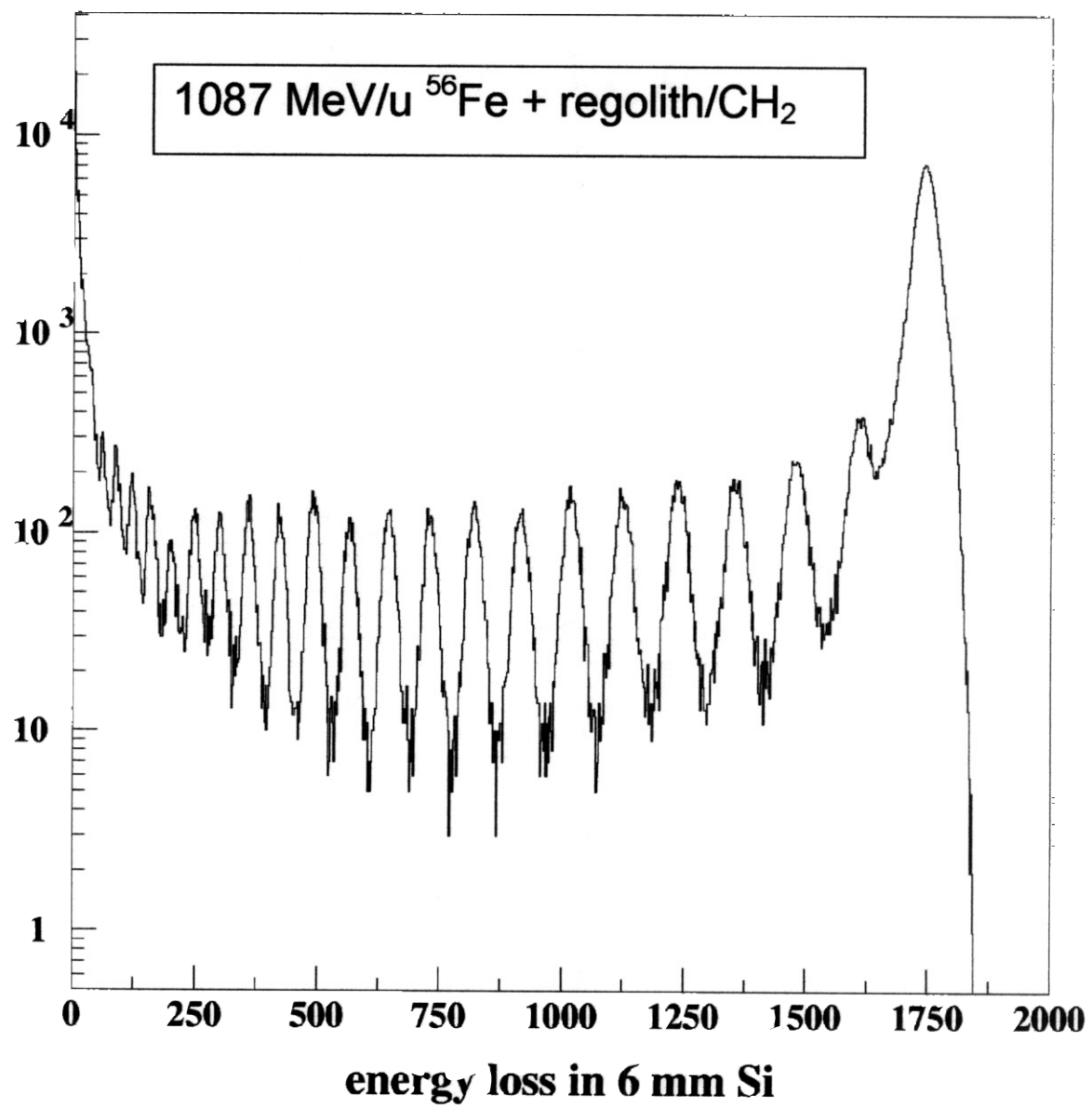


Figure 5. Same as Fig. 4 for a 1087 MeV/u ^{56}Fe beam.

SPACE- AND GROUND-BASED CRYSTAL GROWTH USING A BAFFLE (CGB)

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CGB is the parent investigation to the Microgravity Science Glovebox Investigation “SUBSA” which is scheduled for launch on May 31, 2002. The CGB investigation aspires to eliminate buoyancy driven convection and thus enable reproducible diffusion-controlled crystal growth in space and on earth. The key goals are: (i) obtain a better understanding of the role of convection in formation of inhomogeneities and crystalline defects; (ii) explore solidification phenomena that are obscured by convection; (iii) develop models of the transport processes occurring in solidification; (iv) seek explanations for previous space experiments which did not result in the diffusion-controlled segregation; and (v) measure diffusion coefficients of several dopants.

The focus of the work presented is modification of the existing SUBSA hardware, to meet the scientific goals of the CGB investigation. These modifications include a motor-driven baffle and a higher temperature in the hot zone, to allow growth of Ge and GaSb. Our numerical simulations indicate that Ge and GaSb crystals can be grown in SUBSA thermal chamber with about 300 W of heating power. Therefore, with small modifications of SUBSA hardware, the scientific goals of the CGB investigation could be realized through re-flight experiments in MSG. Using modified SUBSA hardware for the CGB investigation, would result in a significant reduction in cost and preparation time.

To demonstrate that SUBSA hardware can be used for the CGB investigation, a small “model” ground unit furnace was developed at RPI. The ampoule is driven by a linear stepping motor, using a combination of National Instrument’s Lab View and Intelligent Motion System’s IM483 micro-stepping driver. Each micro-step results in 0.05 μm of linear displacement, yielding a smooth steady solidification rate. The baffle is stationary with respect to the thermal chamber, while the ampoule driven linear stepping motor, moves the crystal and the melt relative to the fixed axial gradient.

The design of the RPI model furnace and the preliminary experimental results will be presented. This furnace will be used to grow doped Ge and GaSb crystals under terrestrial gravity and under strong magnetic fields.

Keywords: crystal growth, convection, Ge, GaSb.

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SOLIDIFICATION USING A BAFFLE IN SEALED AMPOULES (SUBSA)

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Solidification Using a Baffle in Sealed Ampoules (SUBSA) will be the first materials science experiment conducted in the Microgravity Science Glovebox (MSG) Facility at the International Space Station (ISS) Alpha. The launch is scheduled for May 31, 2002. Using the specially developed furnace, 10 Te and Zn-doped single crystals of InSb will be directionally solidified in microgravity. A key goal of the SUBSA investigation is to (i) clarify the origin of the melt motion in space laboratories and (ii) to reduce the magnitude of the melt motion to the point that it does not interfere with the transport phenomena. These goals will be accomplished through a special ampoule and furnace design. A disk-shaped baffle, positioned close to the freezing front, is used to reduce melt motion. Furthermore, the solidification will be visualized by using a transparent furnace, with a video camera, continuously sending images to the earth. This allows detection of bubbles and melt de-wetting that could cause surface tension driven convection.

In preparation for the space experiments, 30 ground-based experiments were conducted. The results of ground based tests and numerical modeling will be presented. Based on numerical modeling, 12 mm ID silica ampoules were selected. The small diameter ampoule favors closer placement of the baffle to the interface, without excessive radial segregation caused by forced convection while providing more damping of natural convection. The parts in the silica ampoule include 2 carbon springs made by Energy Science Laboratories, Inc., a pyrocarbon-coated graphite cylinder, pyrocarbon-coated graphite a baffle with the shaft and the InSb charge with the seed crystal grown by W.A. Bonner of Crystallod Inc.

Keywords: crystal growth, convection, Glovebox, InSb.

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ANALYSIS OF CONTAINERLESS SOLIDIFICATION MICROSTRUCTURES IN UNDERCOOLED MELTS AND COMPOSITE SYSTEMS

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Objective and Application to Microgravity Knowledge Base

The main research objective is the evaluation and analysis of the undercooling and resultant solidification microstructures in containerless processing, including drop tube processing and levitation melt processing of selected alloys and composites. The results are intended for use as an experience base for the design of space-based microgravity experiments.

Containerless processing in ground-based drop tubes simulates microgravity conditions via solidification of liquid samples under free fall conditions. The containerless environment is also attained in levitation melt processing and removes a major source of impurities and heterogeneous nucleation sites, allowing for a large melt undercooling. This enhanced liquid undercooling exposes alternate solidification pathways, allowing for the formation of novel microstructures. Controlling the undercooling level provides some control of the operative solidification pathway and the resultant microstructure. The novel structures that may be produced in a ground-based containerless processing facility preview the wide range of possible materials processing experiments that may be conducted in a space-based laboratory. The results of the ground based study will be used to identify critical experimental variables in microgravity processing and the analysis can be used to design and define the science and hardware requirements for extended duration space experiments.

Research Task Description

The ground based program represents a balanced experimental and analysis effort directed toward the investigation of drop tube and levitation containerless processing methods. The investigation focus is on the understanding and analysis of microstructural evolution during solidification of undercooled melts. The liquid undercooling level in a laboratory scale (3 m) drop tube and levitation melting system can be altered through the variation of processing parameters such as alloy composition, melt superheat, sample size and gas environment. The solidification behavior is evaluated through metallography, thermal analysis and x-ray diffraction in conjunction with calorimetric measurements of falling droplets and a heat flow model of the processing conditions to judge the sample thermal history. A central component of the current program addresses the use of containerless processing together with an undercooled melt containing incorporated particles to develop a critical evaluation of solidification front-particle interaction.

Undercooled Melts and Composite Systems

Bulk Undercooling Behavior and Analysis

A typical bulk undercooling response can be illustrated by a recent example: Multiple single droplet DTA experiments on glass encased pure Gold (Au, 99.9999%) have shown that the undercooling response of

Keywords: undercooling, solidification, microstructure, composite materials, new research

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the sample upon repeated melting and freezing under Argon-flow (figure 1) can be separated into two phases. During the initial transient phase the undercooling, ΔT shows a sigmoidal dependence on the cycle number and increases from essentially zero to more than 200 K after about 25 cycles. Thereafter, the sample starts to crystallize at undercooling values between 205 K and 210 K. The measured undercooling values are however lower than the theoretical limit for homogeneous nucleation. Therefore, heterogeneous nucleation kinetics analysis has to be applied for an analysis of the data.

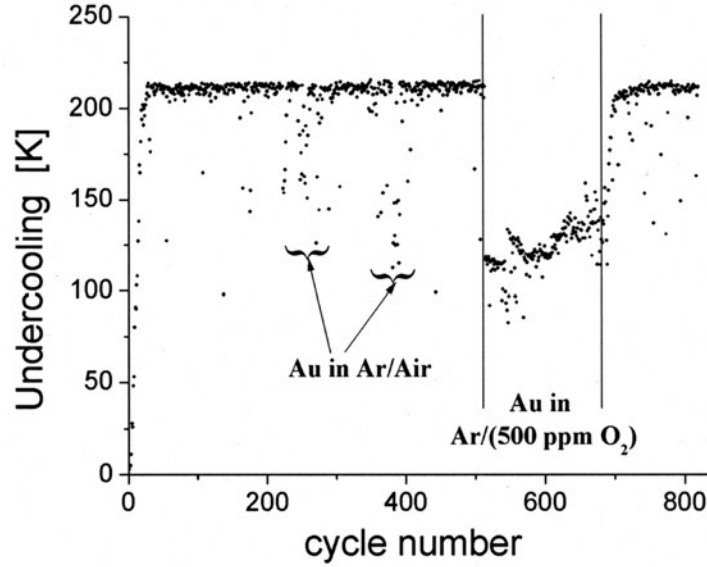


Figure 1. Undercooling of a single droplet of gold as a function of the number of freezing cycles. Increasing the oxygen content in the DTA atmosphere caused a marked reduction in the undercooling.

In DTA measurements, a signal corresponding to a phase change of the material has to exceed an apparatus dependent sensitivity that is approximately constant over a wide temperature range. Therefore, equal nucleation rates can be assumed to be effective at different undercooling values to yield a similar DTA signal that is just detectable. For heterogeneous nucleation the nucleation rate, J_{het} , is given as:

$$J_{het} = \Omega \cdot \exp\left(-\frac{\Delta G_{hom}^* \cdot f(\theta)}{k_B \cdot T}\right) \quad (1)$$

$$\Delta G_{hom}^* = \frac{16\pi \cdot \sigma^3 \cdot T_f^2}{3 \cdot \Delta H_f \cdot \Delta T^2}, \quad \Omega = \rho \cdot v$$

with the catalytic factor, $f(\theta)$, the Boltzmann-constant, k_B , the interfacial energy between solid and liquid, σ , the melting temperature, T_f , the melting enthalpy, ΔH_f , the nucleation site density, ρ and the attempt frequency, v . The linear increase of the undercooling covering almost 200 K leads to the assumption that a fraction of (identical) nucleation sites is removed during each melting-solidification cycle (i.e. by the fluxing action of the glass slag) thus decreasing the nucleation site density. Therefore, the ratio of the (equal) nucleation rates at two different undercooling levels ΔT_1 and ΔT_2 within the initial transient of figure 1 is:

$$\frac{\rho_2}{\rho_1} = \exp\left(\frac{A}{T_2 \cdot \Delta T_1^2} - \frac{A}{T_1 \cdot \Delta T_2^2}\right) \quad (2)$$

$$A = \frac{16\pi \cdot T_f^2 \cdot \sigma^3 \cdot f(\theta)}{3 \cdot k_B \cdot \Delta H_f^2}$$

However, solving equation (2) for the ratio of site densities assuming a nucleation barrier $\Delta G_{\text{het}}^* = 50 k_B T$ at 200 K undercooling gives an unreasonable small value of $\rho_2/\rho_1 = 10^{-59}$. This analysis indicates, that a mere reduction of the number of (equally potent) nucleation sites can not account for the observed increase of the undercooling, but that another mechanism involving a modification of nucleation sites during the initial cycling has to be considered as the key factor. Additional evidence for this interpretation was obtained by studying the undercooling response of the same Au sample under an increased partial pressure of oxygen during further cycling. The undercooling values showed a much larger scatter and a marked decrease to an average undercooling of about $\Delta T = 160$ K.

This example illustrates the possibility to adjust the undercooling level of a sample accurately under terrestrial conditions by nucleation site modification such that the undercooling of the sample can be used as a probe for the solidification kinetics under microgravity. Detailed nucleation kinetics studies can be performed on such a sample because the nucleation mechanism is defined. The results on the gold sample in figure 1 show that such conditioning of samples, in this case achieved by multiple freezing cycles, is necessary to measure characteristic nucleation undercooling values that are related to a single mechanism. The observed impact of the atmosphere on the undercooling response further highlights the need for accurate ground-based experiment preparations in order to exactly define important parameter tolerances in the initial design of all stages of a space experiment.

Particle/Solidification-Front Interactions

A key experimental capability is the development of methods to obtain high bulk melt undercooling with a reproducible behavior. In the solidification of composites the interaction between the solidification front and particles is central to effective processing. The rapid freezing during undercooled liquid solidification simulates convection-free solidification conditions for such composites in a 1g environment because there can be only negligible settling motion of the particles. Numerous models for the interaction behavior have been proposed, but critical tests are lacking in many cases due to confounding gravitational effects. A common concept in the interaction models is the critical velocity for particle incorporation. Theoretical predictions of the behavior of the particles i.e. if they are either engulfed or pushed, as well as most of the experimental analyses [1-3] have been conducted under the constraint of planar interfaces. Such an idealized boundary condition is unlikely to be realized during application-relevant processes where dendritic patterns are common. In fact, a local destabilization of an initially planar solid/liquid interface caused by the different thermal conductivities and specific heats of the solidifying matrix and the particulate material is inherent to the general solidification process even in directional solidification. The morphology of dendritic interfaces introduces a third mode for the resulting distribution of particles within the solidified sample. Besides engulfment and pushing, an entrapment of particles in interdendritic or intercellular spaces is likely to occur and result in the confinement of the particles at the grain boundaries of the metallic matrix. The current experiments use a novel experimental design based upon an undercooled melt with particles to distinguish particle incorporation effectiveness as a function of undercooling in the presence of a different particle sizes and shapes.

Powders of the pure metals Cu and Ni were mechanically blended with different nonmetallic powders and cold compacted in a hydraulic laboratory press. Levitation melting and differential thermal analysis provided the initial testing routine with respect to the compatibility of the different composite materials. It was found that the composite systems Cu/Al₂O₃, Cu/Ta₂O₅ and Ni/Ta₂O₅ are well suited for the experimental study of the incorporation behavior. In all three composite systems, oxide particles remained within the

sample after melting the metallic matrix. Ta_2O_5 is of special relevance for this study, because it offers one of the highest densities of the stable oxides. Thus, the density driven buoyancy is minimized in the $\text{Cu}/\text{Ta}_2\text{O}_5$ and $\text{Ni}/\text{Ta}_2\text{O}_5$ composites thus simulating buoyancy-neutral experiment conditions in terrestrial settings.

In order to achieve variable undercooling levels before the onset of crystallization, DTA samples were encased in a flux of a borosilicate glass (Pyrex) to clean the surface from uncontrolled but potent nucleation sites such as the native oxides of the matrix metals. Figure 2 shows the DTA curves of $\text{Ni}-\text{Ta}_2\text{O}_5$ (a) and $\text{Cu}-\text{Ta}_2\text{O}_5$ (b) composite samples. For both composite samples, an undercooling, ΔT was observed during cooling. The $\text{Ni}-\text{Ta}_2\text{O}_5$ sample (figure 2-a) crystallized at 1260°C for a $\Delta T=195^\circ\text{C}$ while the $\text{Cu}-\text{Ta}_2\text{O}_5$ composite (figure 2-b) crystallizes at 947°C for a $\Delta T=138^\circ\text{C}$ [4]. The samples studied in this work contain dispersed, crystalline particles, but nevertheless undercool readily by more than 100°C and - as shown in figure 2-a for the case of $\text{Ni}-\text{Ta}_2\text{O}_5$ - even exceed a value of $\Delta T = 200^\circ\text{C}$. Yet, these undercooling levels are less than the maximum values. This result emphasizes the small but not negligible heterogeneous nucleation potency of the particles.

The effect of different levels of undercooling on the resulting microstructure is shown for the $\text{Ni}/\text{Ta}_2\text{O}_5$ composite system in figure 3. The average particle diameter is $3\text{ }\mu\text{m}$. At low undercooling (i.e. $\Delta T = 37\text{ K}$, figure 3-a) the particles are confined in regions at the bottom of the sample. Microstructure analyses on splat-quenched samples have shown that the particles are distributed homogeneously inside the liquid sample. Thus, the microstructure shown in figure 3-a is a result of particle movement (pushing) produced by the moving solidification front. In contrast, figure 3-b shows an approximately homogeneous distribution of particles throughout the sample. A fraction of particles are confined at grain or cell boundaries, but

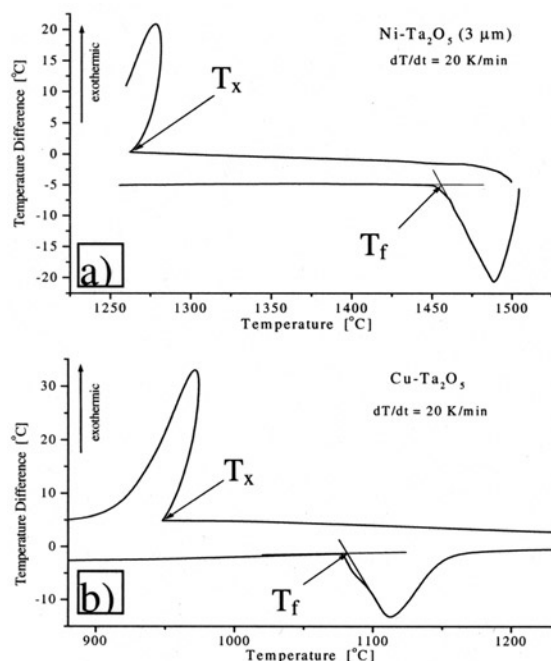


Figure 2: DTA-heating and cooling curves for glass encased (a) $\text{Ni}-\text{Ta}_2\text{O}_5$ and (b) $\text{Cu}-\text{Ta}_2\text{O}_5$. Heating and cooling rates were 20 K/min .

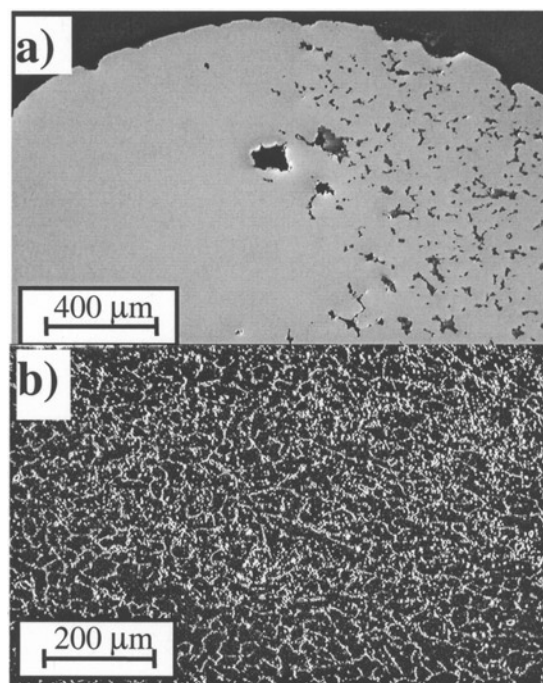


Figure 3: The polished cross-section of $\text{Ni}-\text{Ta}_2\text{O}_5$ -composite samples which undercooled by (a) 37°C and (b) 194°C . Micrograph (b) was taken by using polarized light.

many particles can also be found inside grains. This microstructure indicates that particle engulfment into the dendritic solidification front has occurred at the growth velocity that corresponds to an achieved undercooling of $\Delta T = 194$ K. Incorporation models based on the thermal conductivity criterion [5] and the heat diffusivity criterion [6] predict that Ta_2O_5 particles are pushed during the solidification of both matrix metals. The same result is obtained for many combinations of metal matrix composites because of the low thermal conductivity and the usually lower density of the reinforcement particles relative to the metallic matrix. This prediction is in contrast to the experimental results obtained for the composites that contain Ta_2O_5 . The transition from particle pushing at lower undercooling (i.e. the lower growth velocities) to engulfment at larger rates of the interface movement (i.e. undercooling larger than $\Delta T \cong 90$ K) corresponds to the basic assumption of the incorporation models in references [7-9]. The experiments on the Cu/ Ta_2O_5 composite revealed qualitatively the same dependence: pushing at smaller undercooling and engulfment at $\Delta T \geq 60$ K of undercooling. This result, that large undercooling levels in the presence of particles can be achieved, provides a suitable means to study the interaction of free dendrites with incorporated particles at variable growth velocities excluding the influence of thermal convection inside the liquid matrix. Therefore, undercooling experiments on metal matrix composites under 1 g provide an experience base for future space experiments, where the particle/solidification-front interaction can be studied under convection-free but application related conditions.

The maximum critical velocities as functions of the particle radius were calculated for the Cu/ Al_2O_3 composite system according to relations presented in references [7-9]. The calculated critical velocities for the particle sizes which were used for the experiments ($1.5 \mu m < R < 55 \mu m$) are in the range of 10^{-3} to 10^{-5} m/s. Thus, the average critical velocities according to existing models are much less than 1 cm/s. Critical velocities of the same order of magnitude were calculated for the Ta_2O_5 -containing composites. From given experimental data for the growth velocity of pure Ni [10] and pure Cu [11] as functions of undercooling, the critical undercooling, ΔT_c , which corresponds to the calculated critical interface velocities for particle engulfment have been derived. The ΔT_c values are less than 5 K for all the composites studied. Thus, according to the kinetic models and in contradiction to the experimental results, engulfment should have taken place in all of the systems at the observed undercooling. The large difference between experimental and theoretical values can not be explained by the uncertainty of the materials parameters. Evidence for the large growth velocities at the attained undercooling levels has been obtained by containerless undercooling experiments using electromagnetic levitation (a short, bright recalescence flash was observed). Experimental data for the growth velocity of undercooled metal-matrix composites does not exist. However, experience indicates that the growth velocity of a levitated sample at the undercooling observed is well in excess of 1 m/s. Quantitative measurements of the growth velocity dependence on undercooling in composite systems are necessary for a complete evaluation.

The current studies have established that large undercooling levels in the presence of particles can be achieved and provide a suitable means to study the interaction of free dendrites with incorporated particles at variable growth velocities excluding the influence of thermal convection inside the liquid matrix. The interaction of a fast-moving, dendritic solidification front with dispersed particles during solidification processing of metal-matrix composites have revealed a mode of the incorporation behavior that is not included in existing models and has not been experimentally accessed previously. Detailed studies of the effects of different experimental factors are now in progress to yield a clear understanding of the particle/solidification-front interaction that is needed to evaluate analytical models. Computer modeling of the DTA signals (e.g. Figure 2) measured during solidification processing will compliment the analysis

of the incorporation process. These studies will provide a database for future space experiments where the incorporation behavior can be analyzed under various conditions in the absence of the detrimental influence of convection. The combination of ground-based studies and experiments under microgravity conditions will provide an understanding of the key parameters of the incorporation process that can also lead to improved processing strategies.

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MONTE CARLO METHODS IN MATERIALS SCIENCE BASED ON FLUKA AND ROOT

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Introduction

A comprehensive understanding of mitigation measures for space radiation protection necessarily involves the relevant fields of nuclear physics and particle transport modeling. One method of modeling the interaction of radiation traversing matter is Monte Carlo analysis, a subject that has been evolving since the very advent of nuclear reactors and particle accelerators in experimental physics. Countermeasures for radiation protection from neutrons near nuclear reactors, for example, were an early application and Monte Carlo methods¹⁻⁸ were quickly adapted to this general field of investigation.

The project discussed here is concerned with taking the latest tools and technology in Monte Carlo analysis and adapting them to space applications such as radiation shielding design for spacecraft, as well as investigating how next-generation Monte Carlos can complement the existing analytical methods⁹ currently used by NASA. We have chosen to employ the Monte Carlo program known as FLUKA¹⁰⁻¹¹ (A legacy acronym based on the German for FLUctuating KAscade) used to simulate all of the particle transport, and the CERN developed graphical-interface object-oriented analysis software called ROOT.¹²⁻¹³ One aspect of space radiation analysis for which the Monte Carlo's are particularly suited is the study of secondary radiation produced as albedoes¹⁴ in the vicinity of the structural geometry involved.

This broad goal of simulating space radiation transport through the relevant materials employing the FLUKA code necessarily requires the addition of the capability to simulate all heavy-ion interactions from 10 MeV/A up to the highest conceivable energies. For all energies above 3 GeV/A the Dual Parton Model¹⁵⁻¹⁶ (DPM) is currently used, although the possible improvement of the DPMJET event generator for energies 3-30 GeV/A is being considered. One of the major tasks still facing us is the provision for heavy ion interactions below 3 GeV/A. The ROOT interface is being developed in conjunction with the CERN ALICE (A Large Ion Collisions Experiment) software team through an adaptation of their existing AliROOT (ALICE Using ROOT) architecture. In order to check our progress against actual data, we have chosen to simulate the ATIC¹⁴ (Advanced Thin Ionization Calorimeter) cosmic-ray astrophysics balloon payload as well as neutron fluences in the Mir spacecraft¹⁷. This paper contains a summary of status of this project, and a roadmap to its successful completion.

A Comparison of Monte-Carlo-based Codes

Since the 1960's many different radiation transport simulation codes¹⁻⁸ have been developed. Such diversity is a result of the wide variety of applications for which these codes are employed. Software strategies derive from both *analytic* methods⁹ and *Monte-Carlo* methods^{1-8,10-20}. Uses range from the estimation by NASA of flight crew radiation doses¹⁷⁻²² and the related problem in cancer treatment

Keywords: Monte Carlo, cosmic rays, space radiation, albedoes

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of determining a delivered therapeutic radiation dose, to the evaluation of data in accelerator-based elementary particle physics experiments^{1-2,4,8,11-16} and even extending to the design of instruments for use in cosmic-ray astrophysics¹⁴. The Monte Carlo method is adopted here, having become widely used in the field of experimental particle physics because it represents the best approach to include the widest range of physics and the greatest sensitivity to geometry.

The present project has as its goal the development of a new integrated Monte-Carlo software package specifically tailored for use in the simulation of the space radiation environment. It is intended to address design problems, astronaut dosimetry calculations, and astrophysical payload development. A principal goal is to determine the applicability of such a Monte-Carlo-based computer simulation of the space radiation environment to NASA's Human Exploration and Development of Space (HEDS) enterprise. The new code is based upon the melding together of two existing software packages, the FLUKA,^{1,2,4,10-11} radiation transport program and the object-oriented physics analysis infrastructure ROOT¹²⁻¹³. We have reported elsewhere¹⁷⁻²⁰ on preliminary results and only recent developments are discussed here. The acronym for this investigation is FLEUR (FLUKA Executing Under ROOT) with additional information at our websites.²³

An older Monte Carlo code known as GEANT (GEometry and ANalysis Tool) is still in use. This code was frozen by CERN approximately one decade ago as GEANT3.21, and a new object-oriented version known as GEANT4 is under current development. A recent CERN benchmark comparison of GEANT4 against hadronic interaction data,²⁴ however, suggests that its progress will be slow. Nevertheless, the AliROOT software concept we discuss below is being developed with the intent to seamlessly imbed GEANT3, GEANT4, and FLUKA within its architecture – allowing the user to select the desired transport engine as these become available. At the present time, only FLUKA has been modified to do the full heavy ion transport in an integrated way, although hybrid strategies are being used elsewhere such as at the RHIC²⁵ (Relativistic Heavy Ion Collider) where GEANT3.21 has been used in conjunction with the HIJING⁸ event generator for limited collider applications.

Ongoing FLUKA modifications

The FLUKA authors are committed to the development of a version of the code that includes the complete range of heavy-ion interactions that are needed to simulate the propagation of heavy cosmic rays. However, they presently require manpower assistance to facilitate that implementation in a timely fashion and they have agreed to allow us to provide such assistance. As a result of our support, FLUKA is now available with an embedded version of the heavy ion event generator known as DPMJET which is based on the Dual Parton Model.¹⁵⁻¹⁶ Above 30 GeV/A and on up to air shower energies, we are satisfied that this version of FLUKA well represents the physics. However, the transition region between 3-30 GeV/A is still potentially subject to some improvement in terms of fits to existing data, and below 1-3 GeV/A there are currently no reasonably acceptable comprehensive models.

The current version of FLUKA, which provides a full simulation of heavy-ion inelastic collisions with lab energies above 3 GeV/A, will be further improved by either modifying the existing DPMJET software now present in FLUKA as Version II.5,¹⁶ or the version of FLUKA containing DPMJET III.0 that is about to be released.²³ The simulation of collisions below 3 GeV/A is more problematic and will require considerable effort as part of the NASA Code U investigation of nuclear fragmentation and spallation physics at those energies during the next decade. We hope to participate as part of this future collaborative effort with other groups in the development of accurate models based upon a careful assessment of all of the existing data.²⁶⁻²⁷

In the interim, in order to deal with the lower-energy heavy-ion interactions, we are currently exploring the accuracy with which the RQMD (Relativistic Quantum Molecular Dynamics) code²⁹ replicates the existing data down to the limit for inelastic nuclear collisions. If RQMD is deemed to do an acceptable job at these energies, then it will be incorporated into FLUKA in the same fashion as DPMJET has been. We have already determined that such an incorporation can be accomplished, although there are reservations about some of the neglect of nonlocal quantum mechanics used in RQMD's derivation and a lack of understanding of light-cone physics for relativistic Hamiltonians. In the event that RQMD is found to have unacceptable inaccuracies, our fall-back solution would be to extend the Pre-Equilibrium model called PEANUT, which is already employed internally by FLUKA to generate the interactions of singly-charged incident particles on nuclear targets. Both options (PEANUT and RQMD) will probably be made available to the user.

Beyond the physics enhancements needed for heavy ion transport, there has also been substantial progress in the development of 3-D geometry software technology since FLUKA was first designed. Driven by computer graphics developments and ray-tracing applications, many new 3-D geometry packages are now available. There is also considerable room for improvement in the user-friendliness of the procedures required to input geometry information into the existing FLUKA input formats. Going beyond such utility changes, one of the potential benefits that may be realized by incorporation of a totally new and different geometric representation includes an increase in the calculation speed during transport propagation simulations, along with the additional bonus of easy access to industry-standard input and graphic display formats. As described below, this task has the potential to take advantage of FLUKA's structure to facilitate such an implementation, once the optimum geometry package is identified.

The major reason FLUKA is not more widely used today is the relatively awkward nature of the present user interface to the code. To address these limitations, one major thrust of our present project is to meld FLUKA together with the recently released physics analysis infrastructure software known as ROOT. This task will require an intimate access to the FLUKA data structures as opposed to the grafting of one code to another as, for example, was required to incorporate the DPMJET code within FLUKA.

In the interim, while we are pursuing an integrated solution, we are supporting several enhancements to the existing software. In particular to aid with the FLUKA input geometry problem, we have been successful at designing a set of software assisted procedures for translating geometry inputs originally coded for use with the more widely used, but less accurate GEANT3.21 directly into FLUKA geometry inputs. This effort was undertaken because GEANT3.21 is so widely used, for example as it is by the RHIC experiments at BNL (Brookhaven National Laboratory).²⁵ It was felt that providing the utility of enabling previous GEANT studies to be converted into FLUKA analyses would be greatly appreciated. With this capability the rich heritage of GEANT3.21 research can now be run with FLUKA¹⁴.

In order to facilitate this conversion capability, as well as to improve the native FLUKA geometry input constraints, we have also contributed to the enhancement of the logical operations that may be specified in the combinatorial geometry input format. While this effort may eventually become moot for our project if an entirely different geometry scheme is ultimately employed, such a change is most likely several years away, and in the interim, our contribution will have a substantial positive impact.

ROOT, A Data Analysis Infrastructure

ROOT is based upon Object-Oriented (OO) data structures, a utilization of OO programming that allows many difficult tasks with multiple functions to be done only once. For example, after the work of introducing the complex geometry of an object such as the International Space Station (ISS) is complete, that same information can be used seamlessly as the input for subsequent Monte Carlo calculations. The same data structure can also be applied to visualizations of individual Monte Carlo events in a fly-through 3-D event viewer (Figure 1a), or for choosing regions to provide plots of individual summed quantities of interest. It can be employed for analysis or display applications that need to specify or depict some portion of the geometry involved, or the entire structure. A strong feature of ROOT is that much of the manipulation is provided via GUI (Graphical User Interface) menus, displays, and simple editing features (Figure 1b). Furthermore, when special features need to be added, ROOT uses C++ as a scripting language. This implementation of the scripting language allows the user to create structures and functions that blend naturally into the ROOT architecture, while providing the user a customized extension of the system. In addition, an intelligent pre-processor completely solves the problem of persistency of objects in disk storage. ROOT features and examples can be viewed on the Web (<http://root.cern.ch>), and that site contains the downloadable software with accompanying tutorials.

Within C++, one is allowed to define transportable data structure objects called classes. One advantage of adopting ROOT is that the large and growing community of users is continually developing new classes. These are distributed in an open source model similar to that employed by the developers of the Linux operating system. This permits users to incorporate the new developments of others rapidly into their own customized codes. As different groups begin to utilize this software structure for space radiation simulation, it is anticipated that an exchange of well-documented libraries containing such additions will become commonplace.

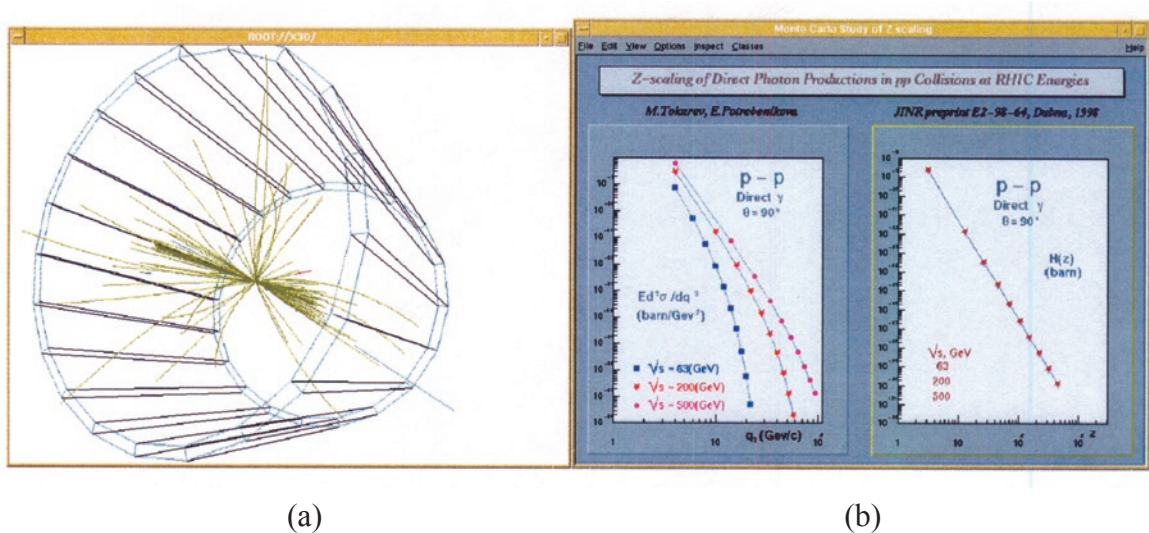


Figure 1. (a) Example of a 3-D event viewer of ATLAS produced by a Monte Carlo simulation (FLUKA/ROOT) with full rotation and zoom capability using only a mouse. (b) Examples of log-log plotting and fitting of data in ROOT.

ROOT is a software package whose scope and capability is much more easily understood by example rather than by a textual description. The following section describes AliROOT (ALICE using ROOT), which is an example of an adaptation of ROOT to control and evaluate Monte Carlo simulations of the

ALICE experiment at CERN. This existing code is serving as a starting point for the FLEUR space radiation simulation code.

AliROOT and the Virtual Monte Carlo Interface

Given ROOT's strengths as a data analysis infrastructure, it is natural to consider developing a general Monte Carlo radiation transport interface. One can break down the general problem of simulating the transport of radiation through a complex geometry into six basic steps:

- a) Inputting the geometry including the specification of the material elemental composition of each sub-volume;
- b) Inputting the incident flux form;
- c) Setting up the desired scoring;
- d) Initializing the transport code as required for the materials and options to be used;
- e) Specifying the number of incident particles to be included in the run;
- f) Executing an event transport cycle for each incident particle during which the specified scoring is done as required.

The information needed by the last cycle, the transport cycle, from the earlier input steps is typically included in one or more files. ROOT is ideally designed to allow the construction of GUI-based tools to accomplish these steps. AliROOT has introduced the concept of a VIRTUAL Monte Carlo Interface, and it

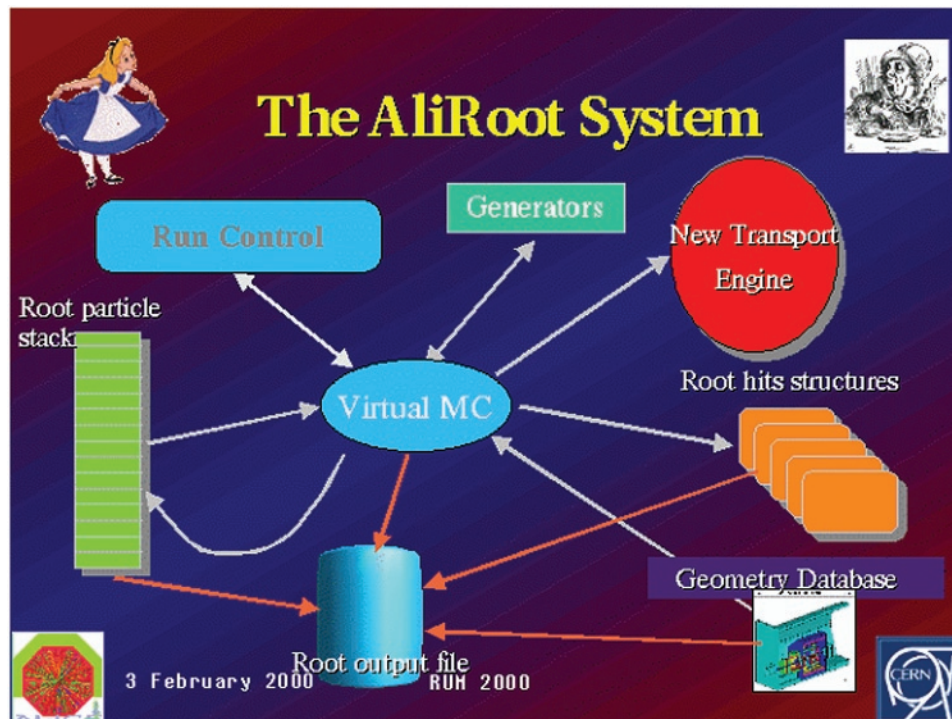


Figure 2. Functional schematic of the ALIROOT architecture.

is in the last step that the features of VIRMCI come into play (Figure 2). During the transport process, as particles move from one sub-volume to another, interactions are determined by reference to known cross-sections appropriate for the composition of each sub-volume. When secondary particles are produced in these interactions, they are pushed onto a stack for subsequent transport after the original incident primary is followed to its eventual end. In each sub-volume, any desired scoring can be done. As an example, the

total energy deposited in that sub-volume by the current particle can be calculated and added to the output data bin for that sub-volume.

The VIRMCI requires that the transport code have the ability to break out at each point where scoring needs to be accomplished to allow that it be done in ROOT data structures. This process can be facilitated if the core data structures of the transport program itself can be mapped directly into ROOT. In the case where the Monte Carlo code is written in FORTRAN, as is FLUKA, utilities exist to enable the direct conversion of FORTRAN common blocks into C++ classes. This means a great saving in execution speed because the internal Monte Carlo values do not have to be passed back to the ROOT-based routines as arguments. Rather, the ROOT-based code will have direct access to any of the transport code's data structures for use in scoring. Thus, one can employ the FLUKA transport code to simulate the physics, and use ROOT-based code to set up the needed FLUKA input files as well as to score the parameters of interest during the simulation. The additional benefit is that the scored events can be examined in ROOT in real-time during the execution of the simulation and the power of ROOT is available to conduct any desired analysis.

In FLUKA, it turns out that the geometry is also dealt with in a sufficiently modular way that it can be broken out and analyzed externally to do the physics calculations. This is because at each spatial step, FLUKA enters a specific set of routines that simply advise the physics calculations what material the present sub-volume is composed of and how far the current particle can go in that sub-volume, given its direction of travel, before its trajectory intersects a boundary of that sub-volume. This allows one to potentially substitute an external geometry package for the internally provided FLUKA geometry package. Currently, such substitute packages exist that allow FLUKA to be run using GEANT4 geometry files internally for these distance calculations. Since translators exist to convert GEANT3.21 geometry into GEANT4 geometry, one can already effectively choose to run FLUKA with any of these geometries. ALIROOT takes advantage of these capabilities, and we hope to be able to explore the possibility of additional geometry packages optimized for particle transport to increase the execution speed of the code. In combination with the GEANT3.21-to-FLUKA converter mentioned earlier, there exist several techniques for translating the geometry databases into the Virtual Monte Carlo shown in Figure 2.

In the current version of AliROOT, the major effort is directed at the creation of generic scoring capabilities. Little attention has gone into input interfacing. Typically, one still edits the original input file with a text editor and then specifies that file through a ROOT macro. Our intention is to add the capability to edit the contents of the required input files directly from ROOT GUI menus and dialogue boxes. This will free the user from having to learn the input file syntax, and can insure that mutually conflicting choices are protected against.

Although not strictly part of the Monte Carlo codes themselves, analysis and display of the data are another strong attribute of AliROOT. Event displays can plot depictions of the trajectories superimposed on the geometry. Full 3-D images can be zoomed, rotated, and edited (Figure 1a), allowing for strong visual analysis tools. Conventional histogramming where the plotted events can be subjected to any number of filters is also routinely possible. These and other tools are a natural consequence for AliROOT and are planned for FLEUR.

Status of the Current Project Including Recent Testing, and Validation

We have made substantial progress in the forging of the final simulation tool to be produced for NASA. The incorporation of the highest energy nucleus-nucleus interactions within FLUKA has been accomplished and interim solutions at the lowest energies are being actively worked on. We anticipate having a version of FLUKA that includes a first attempt at such an interim solution by the end of the current calendar year. The more general problem of providing an event generator to simulate interactions for all heavy ions of interest in the cosmic-ray flux is formidable. The very fact that NASA has embarked on an associated program to take the experimental measurements necessary for modeling heavy-ion transport and nuclear fragmentation below 1 GeV/A energies is indicative of the importance of addressing this problem. The timeframe for this ambitious project is ~ 10 years. While the use of an interim solution is not perfect, it will allow us to begin exploring the possibilities with the available resolution and based on the currently available data. As the long-term NASA project unfolds, such improvements will be introduced into future releases of our FLEUR software.

Our efforts to begin to provide ROOT-based tools to support interacting with FLUKA is also actively proceeding, although full-fledged incorporation of a version of FLUKA within AliROOT is still some distance away. In the interim, ROOT input aids will be made available and ROOT analysis tools will be provided as well.

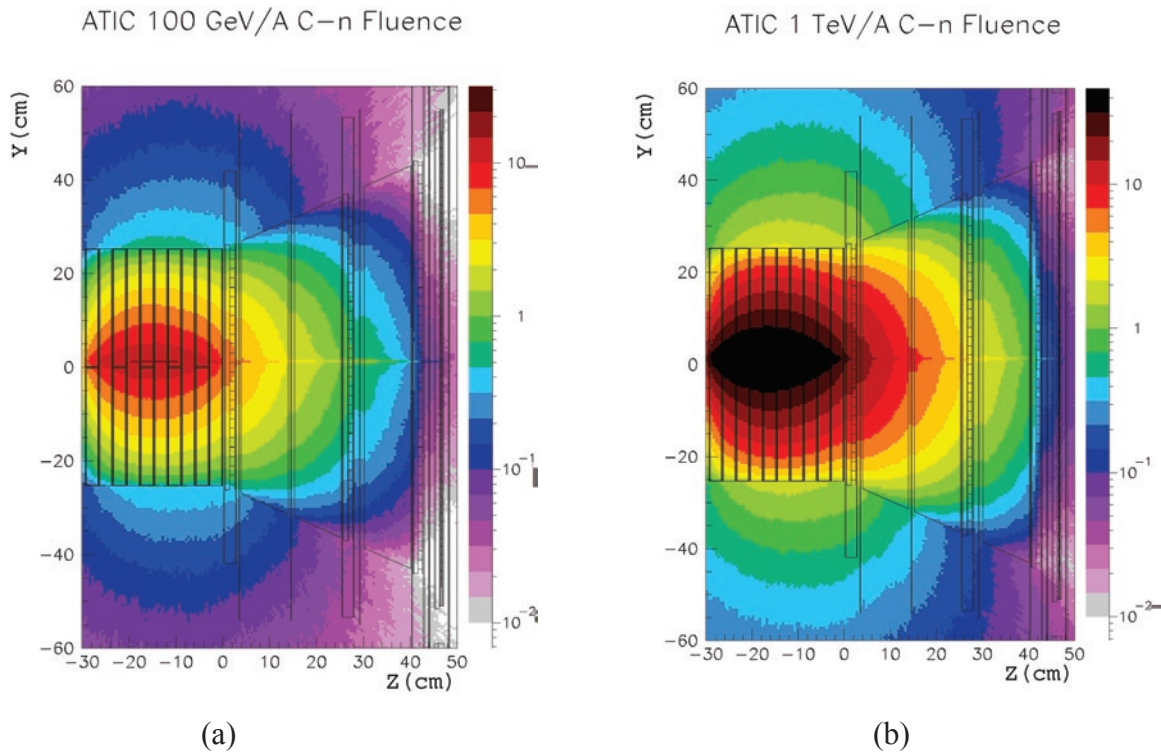


Figure 3. Color plots of neutron fluences due to (a) 100 GeV/A and (b) 1 TeV/A incident carbon in the ATIC experiment as calculated with FLUKA/DPMJET II.5.

In order to validate the present version of FLUKA incorporating the DPMJET code, in order to begin testing the products we have produced we have chosen to perform simulations of the ATIC experiment, a cosmic-ray astrophysics collaboration under the lead of Louisiana State University's Department of Physics and Astronomy.¹⁴ ATIC is a balloon-borne instrument designed to look at the cosmic-ray

composition in the 100 GeV/A to 10 TeV/A range. It consists of a telescope of silicon strip detectors on top of a set of carbon interaction targets followed by a BGO (Bismuth-Germanium-Oxygen, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$) calorimeter, with triggering scintillators interspersed at various points. The experiment was flown near the top of the atmosphere for an extended time in Antarctica during January 2001. Our interest is in determining if FLUKA with DPMJET is sufficient to simulate the actual flight data accurately, and to develop in the process some of the initial ROOT-based analysis tools that will become part of the eventual final package.

As an example of this simulation testing, Figure 3 displays a fluence plot of some of the FLUKA results for a study of the neutron backscatter albedo within ATIC.¹⁴ It represents the total neutron fluence through a raster of pixels due to 1000 simulated 100 GeV/A carbon nuclei normally incident along the central axis of the experiment, and 1600 similar events at 1 TeV/A. An outline of the ATIC hardware geometry is superimposed on the plot. The color-coded levels are logarithmic and represent 6 levels per decade. Fluence is the net flux (time integral of flux) and is expressed as the total path-length density of neutrons

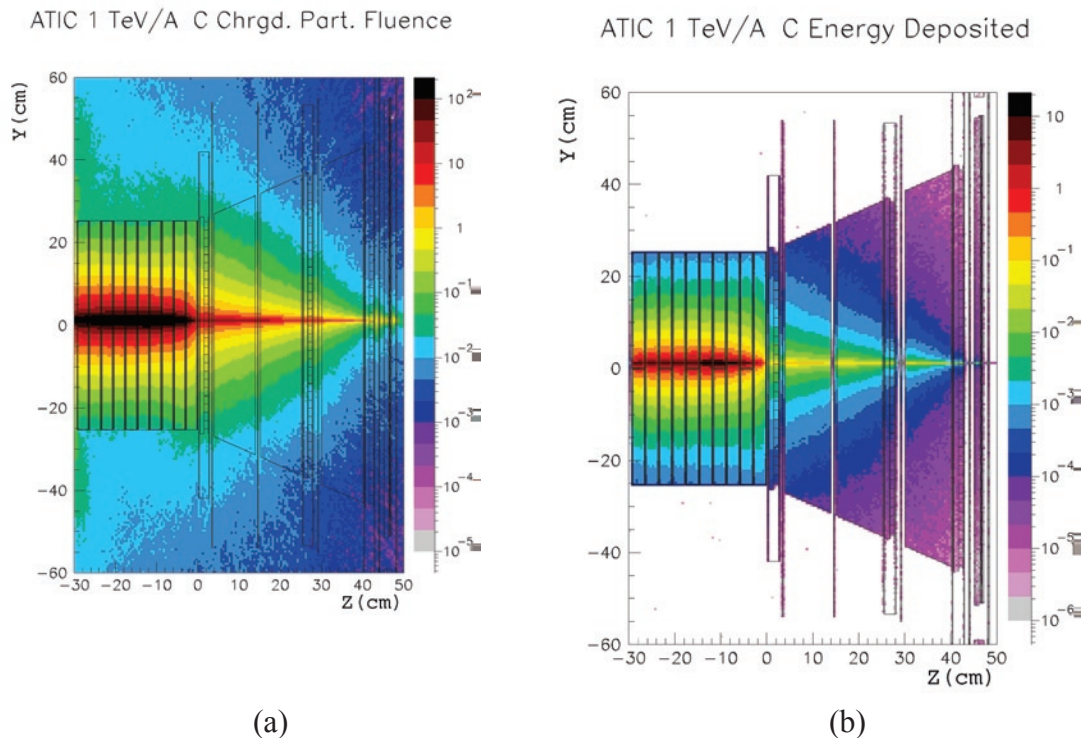


Figure 4. Color plots of (a) charged particle fluences and (b) energy deposited for 1 TeV/A incident carbon in the ATIC experiment as calculated with FLUKA/DPMJET II.5.

of all energies through each pixel. One can use this plot to evaluate the possibility for neutron backscatter contamination in the entire detector from events of this type. Such contamination represents a potential background that must be accounted for in the design of the instrument and it may affect triggering schemes as well as the interpretation of certain data. Additional FLUKA plots from the ATIC study are shown in Figure 4.

As another illustration of the utility of Monte Carlo methods, Figure 5 depicts results from our study already published.¹⁷ These early studies utilized FLUKA for the purpose of producing radiation dosimetry

fluences in a phantom model of the Russian MIR spacecraft. The MIR was represented by a surrounding cylinder of variable thickness, and the shielding was defined as a probability of equivalent thickness of aluminum (an “Al-equivalent”) as seen from the location of NASA, Johnson Space Center’s TEPC, or Tissue Equivalent Proportional Counter.²¹⁻²²

Conclusions

With the advent of new information technology, the tools available for space radiation analysis have shown remarkable improvement. For Monte Carlo methods in particular, what once may have taken weeks to calculate on a large mainframe computer can now be accomplished overnight on an office desktop. The utility of Monte-Carlo-derived fluences illustrated in Figures 3 and 4 becomes evident when one asks the mitigation question: Where is the safe haven from space radiation? In Figure 5, the neutral particles (Figure 5a are neutrons), and the charged particles (5b) are mirror images; if you move to get away from the charged particles then you are bathed by neutrons. Therefore, heavy shielding such as aluminum is not necessarily the answer. Of course, this observation has been known for some time using analytical methods. But the graphics helps us see it. Indeed, the challenge for materials science to come up with materials that will allow the most efficient shielding configurations is a formidable one.

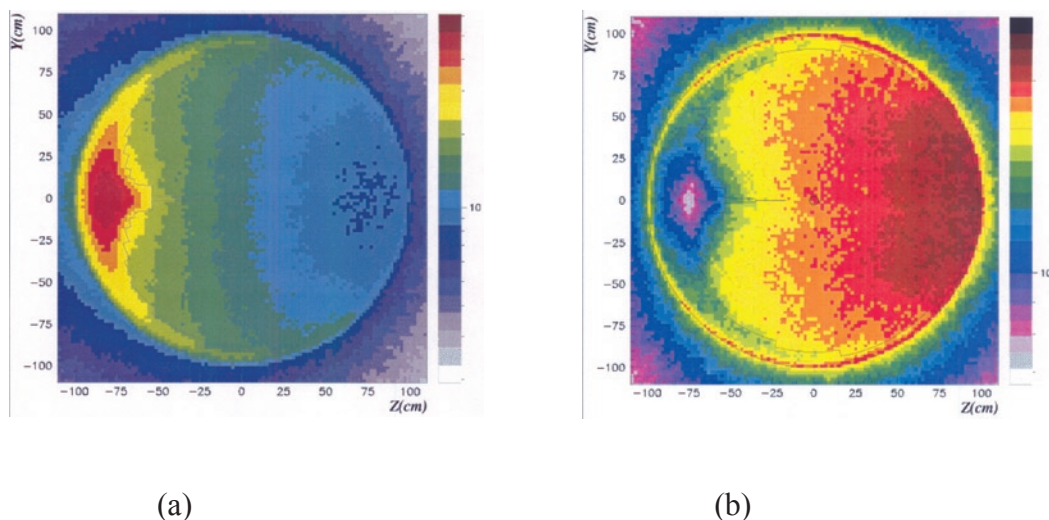


Figure 5. Radiation fluences within and about an Aluminum-equivalent shielding model of the Mir spacecraft, as simulated (in color) by FLUKA and ROOT. (a) On the left is the neutron fluence, and (b) on the right is the charged particle fluence [Ref. 17].

The FLEUR collaboration will continue to adapt the tool of choice in high-energy physics, the Monte Carlo method, to space radiation analysis as our understanding of nuclear fragmentation evolves. In the process, we hope to contribute to the development of mitigation measures for particle radiation by providing a rigorous simulation of all of the relevant physics processes in a full detailed 3-D geometric simulation. As an example, a 10^{15} eV hydrogen ion at the “knee” in the cosmic-ray spectrum is rare (1 event/m²/ster/year), but for the area of the ISS (>365 m²) these events are happening every day. It is not just the primary, incident particle that poses a hazard but also the hadronic cascade with its shower of generations of lower-energy secondary particles that precipitate. The high-energy accelerators such as Fermilab and CERN deal with this subject daily, and we hope to bring their tools into the arena of space exploration as these are being developed.

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COMPARISON OF STRUCTURE AND SEGREGATION IN ALLOYS DIRECTIONALLY SOLIDIFIED IN TERRESTRIAL AND MICROGRAVITY ENVIRONMENTS

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The research is technologically important because it is directly relevant to a casting process used to make critical components that are used in high temperature gas turbine engines in aircraft and land-based power generators. The science learned in this program will enable engineers to better control this important casting process. The grant is a Flight Definition Program, so efforts have been on preparation to eventually conduct long duration experiments in microgravity. The primary purpose is to compare the structure and segregation in a metallic alloy that is directionally solidified in a terrestrial environment (subject to convection) to the same alloy solidified in microgravity. Thermosolutal convection masks the effects of diffusional transport during solidification and also leads to macrosegregates known as freckles; hence, in terrestrial experiments, diffusive and convective phenomena occur simultaneously, which complicate the study of dendritic growth. In microgravity, however, it would be possible to effect directional solidification with no thermosolutal convection. Our hypotheses are the convection and attendant macrosegregation will be eliminated and the dendritic microstructure will be greatly altered in microgravity. Availability of microgravity provides an opportunity to obtain experimental data, where thermosolutal convection is negligible.

Terrestrial solidification experiments on Pb-Sb alloys have been done using different growth conditions to effect different dendritic microstructures. Numerical modeling to simulate the transport phenomena and solidification of the planned experiments and terrestrial experiments are continuing in order to define growth conditions for microgravity experiments. Theoretical models of dendritic solidification rely on the assumption of only diffusional effects, but, on earth, convection is important and may mask the diffusional effects. Thus, from a scientific point of view, it is important to compare the characteristics of directional solidification in both environments. Also attempts to measure the diffusivity of Sb in Pb melts have been done because it is needed to validate dendritic growth models. Pb-2.2 %Sb samples were solidified in 1, 2, and 3 mm ID quartz capillaries at 82 K/cm and 0.4 $\mu\text{m/s}$. Precautions to avoid vibrations and to achieve a rapid quench in He were effected. It was found that employment of ampoule diameters as small as 1 mm cannot eliminate the convection. Calculations indicate that capillaries of less than 0.6 mm may be needed. A finite element model for predicting cellular and dendritic growth forms has also been under development. The numerical model has been tested in a number of scenarios, including the dendritic solidification of hypoeutectic Pb-Sb alloys (2.2 and 5.5 %Sb) under realistic thermal conditions.

Background on Simulating Solidification Microstructures

Significant progress has been made in the simulation of the solidification of single-component crystals [1-13], when heat diffusion is the only transport mechanism. Just recently, models that include convection have also been presented [14-16]. When crystalline anisotropy is included, the models agree with

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solvability theory [17]. To model dendritic solidification, the length scale, D_L/V , is paramount, where D_L is the mass diffusivity in the liquid and V is the solidification velocity. This diffusion length is several orders of magnitude smaller than the heat-diffusion length, which makes numerical approximations to the solution of the governing equations difficult.

Numerical solutions to alloy solidification in one dimension were presented by Rubinsky [18] and Derby and Brown [19]. In Ref. [18], the interface was tracked with an extra node, and the implications of the results on the stability of a plane front were discussed. Derby and Brown [19] used their model to study the one-dimensional solidification of CdTe-HgTe in a vertical Bridgman furnace. Two-dimensional solutions for binary alloys were first sought by McCartney and Hunt [20], Ungar and Brown [21], and Tsai and Rubinsky [22]. McCartney and Hunt [20] assumed a dendrite shape and then chose a mesh with points lying on the interface. The energy and solute equations were solved, the computational mesh was modified to adjust the shape so it was in equilibrium with the new solution, and the procedure was iterated to convergence. Subsequently, the solution of the energy equation was eliminated, and temperature was included through an imposed moving linear temperature field [23]. Ungar and Brown [21] analyzed the stability of a plane front solidifying with a constant velocity under a prescribed temperature gradient. Their method was capable of calculating cellular interfaces, and variations of it were also used in subsequent publications [24-27]. Tsai and Rubinsky [22] developed a finite element model with interface and a moving mesh that was refined at the interface. They studied the effect of temperature-fluctuations on the stability of a planar interface.

Somewhat later, McFadden et al. [28] developed a steady-state finite differences model for the three-dimensional calculation of non-planar morphologies in Al-Cr alloys, assuming a linear temperature field. Palle and Dantzig [29] developed an adaptive mesh finite element method for the solidification of binary alloys, based on a locally refined mesh in the proximity of the interface. The method was applied to two-dimensional solidification of Fe-0.05 wt% C in an under-cooled melt. Juric [30] used a single-field representation for the liquid and solid, in which the jump in material properties at the interface is implicitly included. This method uses a material indicator similar to the phase-field variable. The model was applied to directional solidification starting from a perturbed plane front, and the theory of Mullins and Sekerka [31] was used to ensure that the system was unstable. Simulations, intended to show the formation of dendrites, revealed resolution difficulties so Juric resorted to the assumption of a known linear temperature field to avoid solving the energy equation. Models based on boundary integrals and the solution of an integro-differential equation were proposed in Refs. [32,33] for solving steady-state solidification. Many numerical simulations of dendritic solidification of binary alloys have been done using the phase-field method [34-42]. By this technique, Warren and Boettinger [38] obtained realistic growth patterns that captured the coarsening, and coalescence of secondary and tertiary dendrite arms. In all of these works, however, the temperature field was prescribed, and only the solute concentrations were calculated.

Finite Element Model

In its present state, both the energy and solute conservation equations are solved using finite elements. The energy equation is solved in a fixed mesh, in which the interface is tracked [13]. The solute conservation equation is solved in an independent and variable mesh in the liquid that is very fine at and next to the interface to resolve D_L/V ; it is re-generated at every time step to accommodate the interface. The model has been tested in a variety of situations, including the solidification of Pb-Sb alloys [43]. To date, it is assumed that the thermal properties are different but constant in each phase, the latent heat is constant, and

the densities of the solid and liquid phases are equal so fluid flow by shrinkage or natural convection is ignored. In the proposed research, these assumptions will be relaxed when necessary. There is a continuous temperature across the solid-liquid interface and

$$(\eta Le_S \nabla T_S - Le_L \nabla T_L) \cdot \mathbf{n} = \left[\frac{1}{St} + \beta (T_I - T_m) \right] V \quad (1)$$

In Eq. (1), the subscripts S and L denote the solid and liquid, respectively; $\mathbf{n}$ is the unit vector normal to the interface pointing into the liquid; and V is the local normal interface velocity. The equation is non-dimensionalized using a reference length H , the solute diffusion timescale H^2/D_L , and the characteristic velocity D_L/H . With the dimensional temperature as T^* , the non-dimensional temperature is $T = (T^* - T_E)/\Delta T$, where $\Delta T = T_{m0} - T_E$, T_{m0} is the melting point of the major element, and T_E is the eutectic temperature. Parameters are the ratio of the volumetric heat capacities in the solid and liquid ($\eta = \rho c_{PS} / \rho c_{PL}$), the Lewis numbers ($Le_S = \alpha_S / D_L$ and $Le_L = \alpha_L / D_L$), the Stefan number ($St = c_{PL} \Delta T / L$), and the difference in specific heats ($\beta = (c_{PL} - c_{PS}) / c_{PL}$). D_L is the diffusion coefficient, L is the latent heat, and $\alpha_S = \kappa_S / \rho c_{PS}$ and $\alpha_L = \kappa_L / \rho c_{PL}$ are the thermal diffusivities, with κ_S and κ_L the thermal conductivities. The non-dimensional temperatures T_I and T_m denote the local interface and equilibrium liquidus temperatures, respectively.

Diffusion in the solid is neglected and the concentration in the liquid is solved. At the interface,

$$(-\nabla C_L) \cdot \mathbf{n} = (1 - k) C_L V \quad (2)$$

where C_L is the concentration in the liquid and k is the equilibrium partition ratio. Here the curvature of the interface is twice the usual (as in Kurz and Fisher [44]); numerical determination of the curvature can be found in Ref. [13]. The interface temperature is given by a generalized Gibbs-Thompson relation,

$$T_I - T_m + (1 + m C_L) \sigma \omega + \mu V + \beta St (T_I - T_m)^2 = 0 \quad (3)$$

where ω is a non-dimensional curvature; $\sigma = T_{m0} \gamma / \rho L H \Delta T$ and $\mu = D_L / H v \Delta T$ are non-dimensional interfacial energy and kinetic mobility, respectively; γ is the dimensional interfacial energy; v is the kinetic mobility; and the liquidus is approximated by $T_m = 1 + m C_L$, where m is the non-dimensional slope of the liquidus line. To arrive at Eq. (3), an equation given by Alexiades and Solomon [45] is modified to include the effect of the solute concentration and the term for the kinetic mobility of the interface.

The numerical solution of concentration was via Galerkin weighted residuals, and the time derivative was discretized using the θ -method [46]. The resulting linear equations were solved using conjugate-gradient iterations [47]. Several ways to generate meshes that accommodate the moving interface were considered [48-51]. The decision was made to perform a complete re-meshing of the liquid region at each time step, in order to avoid mesh degradation associated with deformation of the elements [52]. Because meshing must be performed at every time step, efficiency is a key issue. With the exponential decay of the solute boundary layer, quadratic triangular elements are adapted to reduce the error in mass conservation to less than 0.1%. To obtain a computational cost of $O(N \log N)$, the elements of the temperature-mesh are classified using a quadtree [11,53], and the concentration-mesh comprises triangular elements, with a special implementation of the Delaunay method [53]. By subdividing the elements properly, then the number of elements that is bounded and does not depend on the overall size of the mesh [54,55]. For validation, the numerical model was applied to one-dimensional solidification of hypoeutectic Pb-Sb

alloys and compared to an analytical solution in Ref. [45]. The calculated interface-position had a relative error of less than 0.01% throughout the calculation. The calculated and analytical solutions to the velocity of the interface were indistinguishable when plotted together; agreement was within 0.04%.

The result of another one-dimensional calculation is shown in Fig. 1. The domain is long enough to approximate steady-state solidification at 10 $\mu\text{m/s}$. Figure 1 shows the temperature and a region of constitutional undercooling, when the interface is at approximately 10 mm. The change in the gradient at the interface is due to the difference in thermal conductivity between the solid and the liquid and the latent-heat release. The maximum concentration (Fig. 2) differs by only 0.3% from the steady-state value, C_0/k ; the calculated interface velocity deviates by only 0.3% from the steady-state value; and the total solute mass conservation shows no error.

Two-dimensional calculations of equi-axial grains in under-cooled melts have been done for pure metal and a binary alloy [43]. The calculations include an anisotropic interfacial energy and a kinetic mobility at the interface. The pure substance solidifies much faster than the alloy (in this case, about twice as fast). Also the interface shapes are quite different (Fig. 3); the alloy has much thinner and longer grooves. The results of another calculation are shown in Figs. 4a and 4b. Boundary layers are evident (Fig. 4a); also a slight amount of microsegregation in the solid is observed. Initially the concentration of the liquid at the surface of the seed is assumed to be C_0 , which explains the depleted region right next to the starting interface. Figure 4b zooms into the thin long channel at 45 degrees of Fig. 4a and shows the fine detail of the mesh.

The model was also tested in predicting the break-down of planar fronts into cellular morphologies. Conditions similar to those of Ungar and Brown [24] resulted in good agreement at low Peclet numbers. When perturbed, the planar interface responded according to the theory of Mullins and Sekerka [31]. Ungar and Brown [21,24] assumed that solidification was effected in a constant gradient, but here both temperature and concentration are solved. For Peclet numbers of 1 and greater, the shape of our cells differs from that of Ungar and Brown, our grooves are shallower, and the tips are flatter.

For Pb-2.2 wt% Sb, solidified with a temperature gradient of 100 K/cm at a rate of 3.79 $\mu\text{m/s}$, the theory of Mullins and Sekerka [31] predicts a most unstable wavelength of about 10 μm . A mesh that resolved this small length scale was set up. An anisotropic interfacial energy and a constant for the kinetic mobility were used. Figure 5 shows the simulated results up to 26 s after the perturbation, with a wavelength of 40 μm , was applied. Very early there are small wavelets of about 7 μm sitting on the long wavelength of 40 μm . The system evolves to larger structures, and eventually the computational region accommodates the equivalent of only one primary dendrite arm. This calculation indicates that if one wishes to study the evolution of a dendritic structure from a planar interface, then the small-scale instability must be resolved to provide the correct initial conditions. The temperature (not shown) is not constant along a fixed value of x , nor linear in the x -direction along fixed values of y , indicating that models of this type should solve for both temperature and concentration.

A simulation of Pb-5.8 wt% Sb, solidified in a temperature gradient of 100 K/cm is presented next. The calculation was started from a planar front, and a relatively large perturbation with wavelength 0.1 mm was used purposely. Figure 6 shows the solute concentration at 96 s; the position of the interface is white. The solid comprises the primary dendritic constituent and the eutectic constituent. The dendritic constituent

has an average concentration of less than 3.5 wt% Sb, and the eutectic constituent has a concentration very close to the equilibrium eutectic. In this simulation, the morphological features of the eutectic mixture were not calculated.

Directional Solidification in Small Capillaries

It is often believed that convection does not occur during solidification in very small capillaries; our experiments indicate otherwise. Figure 7a shows the macrosegregation along the length of Pb-2.2 wt% Sb alloy in capillaries. C_s/C_o versus fraction distance solidified is plotted, where C_s is the concentration of Sb and C_o is the concentration of Sb in the starting melt. Figure 7b shows the segregation profiles expected from a model by Favier [69] that uses a Peclet number, $\Delta (= \delta R/D_L)$, where δ is the momentum boundary layer thickness, D_L is the diffusivity in the melt and R is the growth speed. The curves correspond to Δ from 0.25 (mostly convective mass transport) to 4 (nearly diffusive mass transport). It is apparent that decreasing the diameter down to only 1 mm did not eliminate convection; rather there is significant convective mixing even in the 1 mm diameter sample. Our numerical simulations show that convection persists even with a diameter as small as 600 μm .

Education and Public Outreach

NASA sponsorship has provided the partial support of post-doctoral students, graduate students and undergraduate students. Graduate students use research results in their M.S. theses or Ph.D. dissertations. The investigators have long records of supervising student-research and including them as co-authors (e.g., Refs. [13,43,57-71]). Since the research is central to the scope of our overall program on casting and solidification, other students benefit because periodic seminars are held, in which the students share their research progress with the entire group.

Prior NASA sponsored-research has led to research and dissemination for the casting industry. In the mid-90s, the UA-investigators and students were part of a DARPA-sponsored research program for the Investment Casting Consortium Arrangement (ICCA). ICCA comprised leading investment casting companies (Howmet and PCC), engine companies (GE and Pratt-Whitney), a software company (UES Software), and others. At UA, our major task was to develop a numerical model for predicting macrosegregation in directionally solidified multicomponent alloys. This was realized because, under the aegis of NASA grants, we had developed a simulator for binary alloys. The collaborator at Pratt-Whitney used the multicomponent version to make “defect maps” for two Superalloys, to predict the thermal conditions for producing castings that are free from the insidious freckle-defects.

Ingot producers and engine companies effect research and development in the Special Metal Processing Consortium (SMPC), centered at Sandia National Laboratories. The member companies are Allvac-an Allegheny Technology Company, Carpenter Technology Corporation, General Electric Aircraft Engines, Precision Rolled Products, Pratt-Whitney, Rolls-Royce Corp., RMI-Titanium, Schultz Steel, Special Metals Corp., and Trimet. The research team at UA has been selected to simulate ingot solidification with the goal of avoiding processing conditions that lead to macrosegregation defects in multicomponent alloys. Again this is possible because it is an outgrowth of the simulator for binary alloys developed under grants from NASA.

In recent years, we added the behavior of gas-forming elements in solidifying alloys. We parlayed our computer program developed under NASA grants and the ICCA contract with a grant from NSF and a contract with Sandia Laboratories. The goal is to use the simulator to mitigate microporosity in

castings. We worked with an investment casting foundry (Wyman-Gordon, since purchased by PCC) and co-authored a paper in a peer-reviewed journal. Three papers on simulating microporosity have been published and presented directly to industry at the American Foundry Society-Casting Congress 2001 and ASM International-Materials Solutions Conference, 2001. A collaboration with Hitchiner Casting Co. to simulate the formation of microporosity in steel castings has been set up, under the aegis of the Materials Corridor Initiative that leverages the partial support of DOE with the support of industry to tackle problems that pertain to the economic sustainability of the USA-Mexico border region. Very recently, a program sponsored by the Air Force Research Laboratory and Howmet Casting Company on simulating the formation of porosity in Superalloy castings was initiated.

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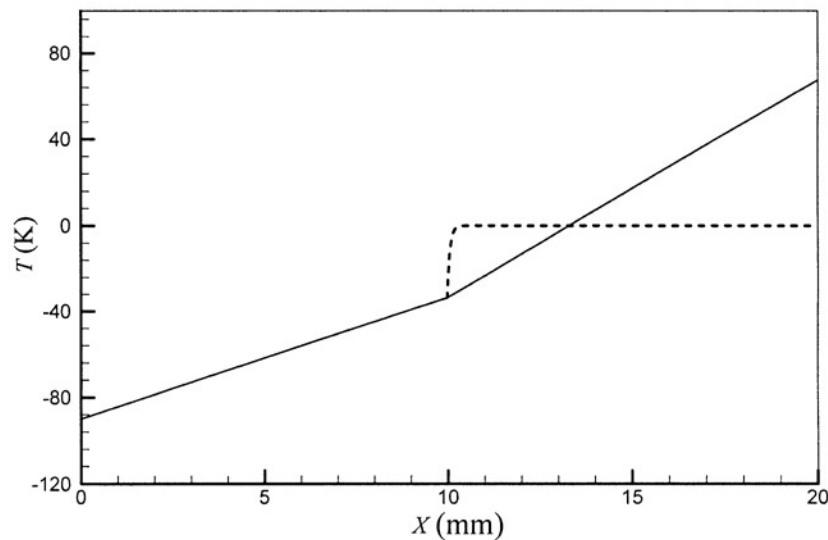


Fig. 1. Simulation of one-dimensional solidification of a Pb-2.2 wt% Sb alloy; the solid lines are temperature; the dashed curve is the liquidus temperature.

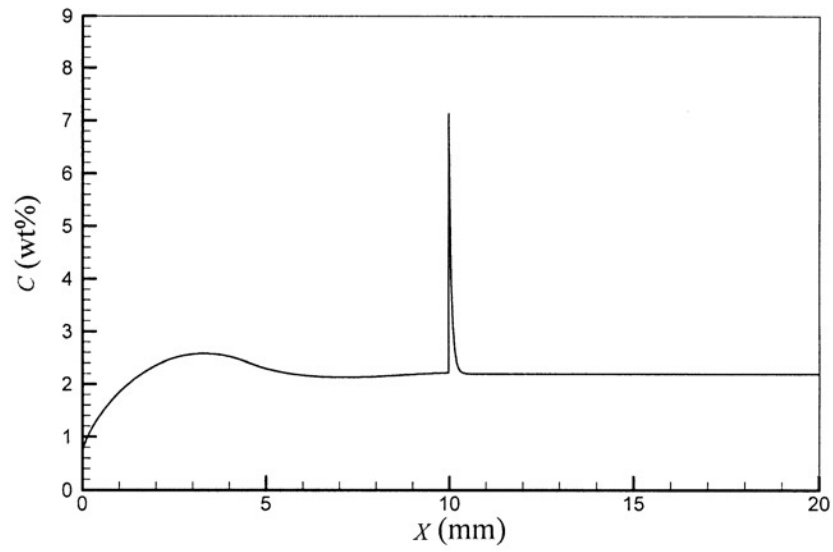


Fig. 2. Concentration profile after steady state solidification is achieved.

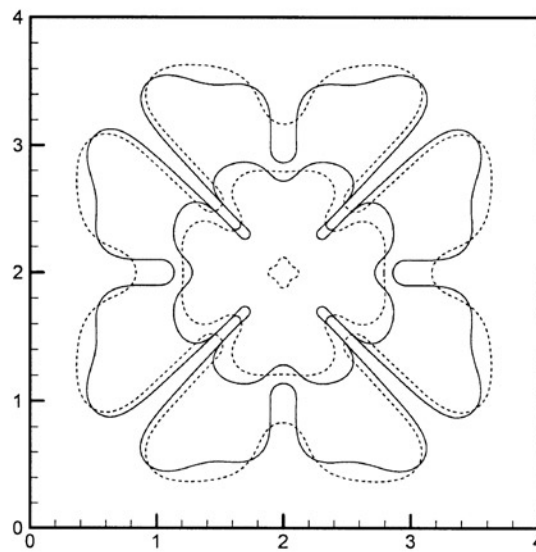


Fig. 3. Simulation of an equiaxial grain in an undercooled liquid: comparison of the morphology of a pure substance (dashed interface) and that of an alloy (solid interface).

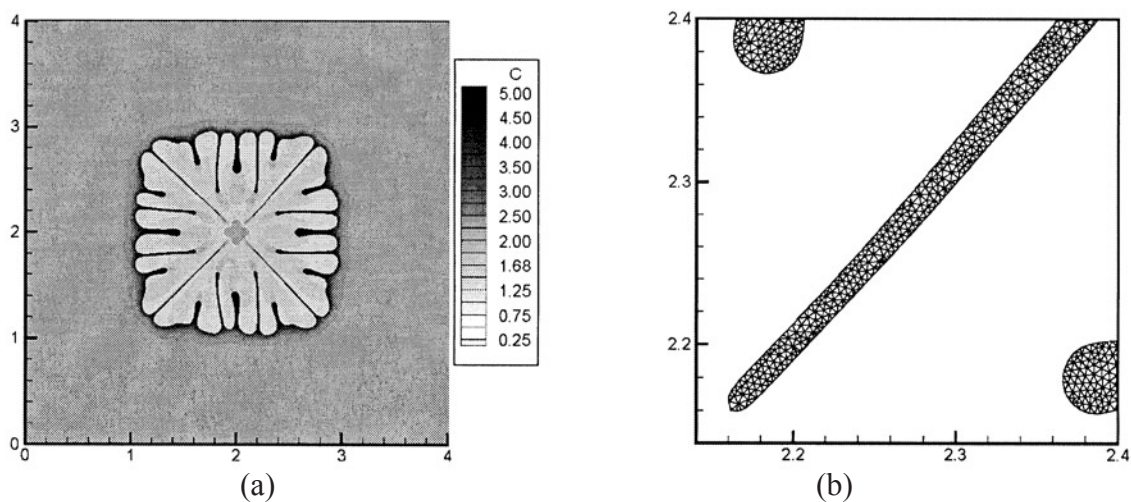


Fig. 4. Simulation of equiaxial growth of an alloy: (a) solute concentration (the seed is shown darker than its concentration kC_0); (b) detail of the adaptive mesh in the narrow channels.

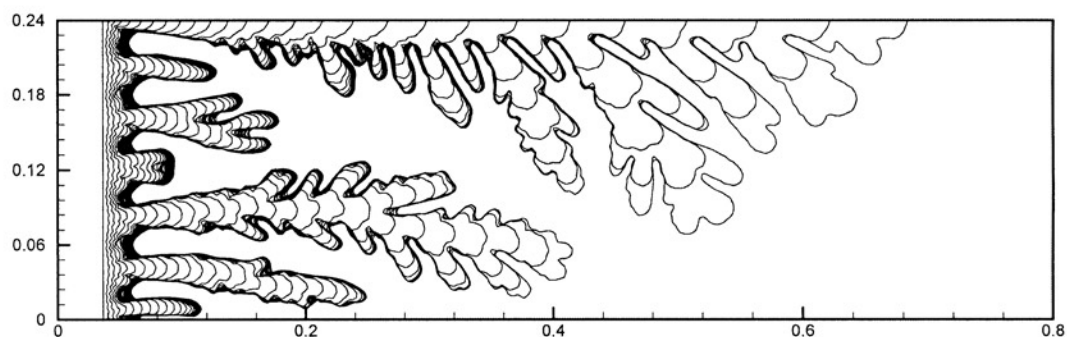


Fig. 5. Solidification of a Pb-2.2 wt% Sb alloy after 26 s; interface position is shown at intervals of 1 s.

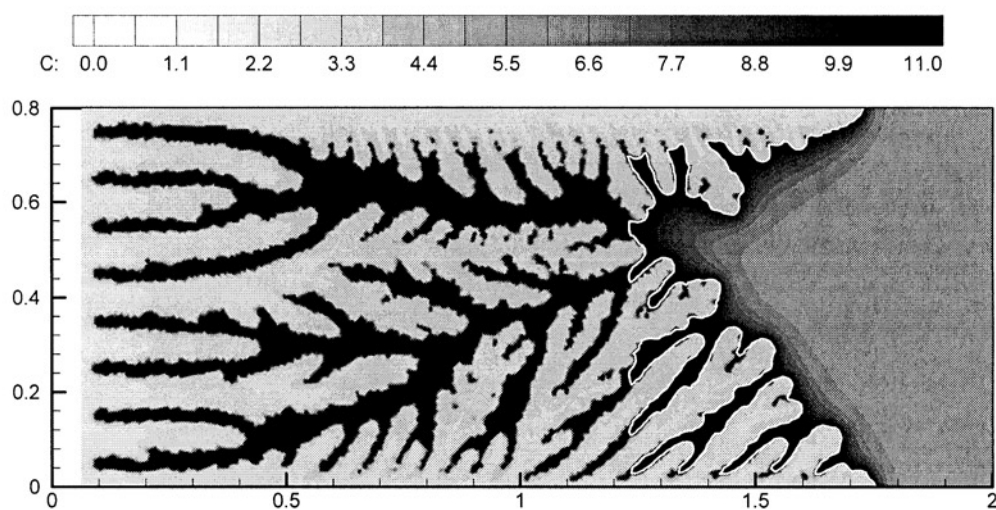
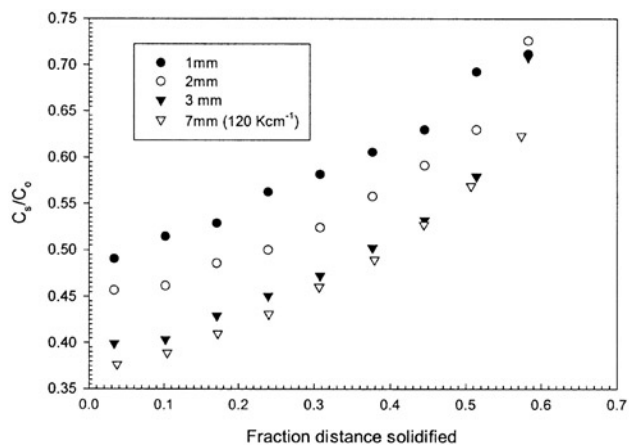
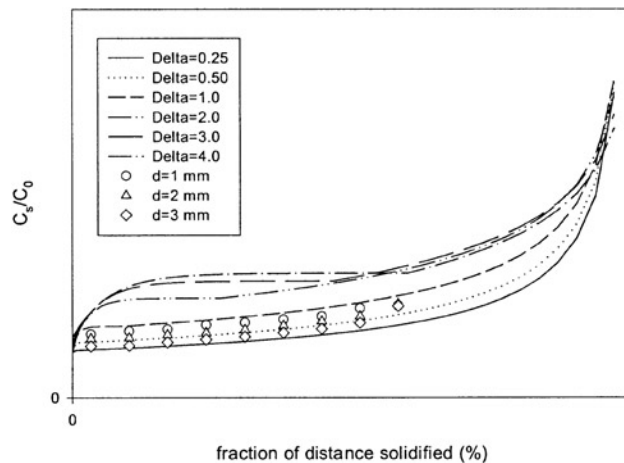


Fig. 6. Sb-concentration during solidification of Pb-5.8 wt% Sb alloy; solid-liquid interface is white.



(a)



(b)

Fig. 7. Macrosegregation resulting from planar solidification of Pb-2.2 wt% Sb: (a) measured; (b) measured and calculated using model of Favier [56].

TRANSIENT INTERFACIAL PHENOMENA IN MISCIBLE POLYMER SYSTEMS (TIPMPS)

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Almost one hundred years ago Korteweg published a theory of how stresses could be induced in miscible fluids by concentration gradients, causing phenomena that would appear to be the same as with immiscible fluids. Miscible fluids could manifest a “transient” or “effective” interfacial tension (EIT). To this day, there has been no definitive experiment to confirm Korteweg’s model but numerous fascinating and suggestive experiments have been reported. The goal of TIPMPS is to answer the question: *Can concentration and temperature gradients in miscible materials induce stresses that cause convection?*

Many polymer processes involving miscible monomer and polymer systems could be affected by fluid flow and so this work could help understand miscible polymer processing, not only in microgravity, but also on earth. Demonstrating the existence of this phenomenon in miscible fluids will open up a new area of study for materials science. As the TIPMPS SCR Panel, December 2000 stated:

“If gradients of composition and temperature in miscible polymer/monomer systems create stresses that cause convection then it would strongly suggest that stress-induced flows could occur in many applications with miscible materials. The results of this investigation could then have potential implications in polymer blending (phase separation), colloidal formation, fiber spinning, polymerization kinetics, membrane formation and polymer processing in space.”

The science objectives of TIPMPS are:

- 1) Determine if convection can be induced by variation of the width of a miscible interface
- 2) Determine if convection can be induced by variation of temperature along a miscible interface
- 3) Determine if convection can be induced by variation of conversion along a miscible interface

An interface between two miscible fluids can best be created via a spatially-selective photopolymerization of dodecyl acrylate with a photoinitiator, which allows the creation of precise and accurate concentration gradients between polymer and monomer (Figure 1). Optical techniques will be used to measure the refractive index variation caused by the resultant temperature and concentration fields. The viscosity of the polymer will be measured from the increase in the fluorescence of pyrene

Because the large concentration and temperature gradients cause buoyancy-driven convection that prevents the observation of the predicted flows, the experiment must be done in microgravity.

In this report, we will consider our efforts to estimate the square gradient parameter, k , and our use of the estimates in modeling of the planned TIPMPS experiments. We developed a model consisting of the heat and diffusion equations with convective terms and of the Navier-Stokes equations with an additional

Keywords: miscible interface, convection, Korteweg stress, polymer, flight

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volume force written in the form of the Korteweg stresses arising from nonlocal interaction in the fluid. The fluid's viscosity dependence on polymer conversion and temperature was taken from measurements of poly(dodecyl acrylate). Numerical modeling demonstrated that significant flows would arise for conditions corresponding to the planned experiments.

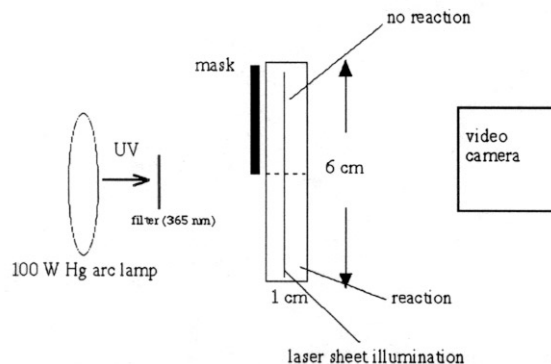


Figure 1. A schematic of the TIPMPS experiment in which UV light and a mask are used to create gradients between dodecyl acrylate and its miscible polymer.

Background

Korteweg proposed in 1904 that a nonuniform concentration distribution leads to stresses in a fluid.¹ Anderson and McFadden modeled internal waves in a near-critical fluid using a Korteweg stress term in the momentum equation.² Joseph and Renardy considered many aspects of Korteweg stresses in miscible fluids.³

A single fluid at equilibrium has a free energy that is constant throughout the volume. The free energy of a nonuniform fluid can be treated by including a term proportional to the square of the concentration gradient. The expression for the free energy at a location is now a functional because it depends on the concentration beyond the location. Cahn and Hilliard developed the theory based on what is often called the Ginzburg-Landau free energy functional, in 1958.⁴

In an earlier work,⁵ we reviewed the work on effective interfacial tension, Korteweg stress and miscible fluids. For systems far from equilibrium, the composition can be nonuniform even if the liquids are miscible. We can write the free energy functional as

$$F = \int_{\Omega} f_0 dx + \sigma A \quad (1)$$

where

$$\sigma = k \int_{\Omega} |\nabla c|^2 d\xi \quad (2)$$

is the effective interfacial tension, and A the area of the interface.

If we consider a linear concentration gradient in one dimension, we can write:

$$\sigma = k \frac{\Delta c^2}{\delta} \quad (3)$$

where δ is the length over which the concentration changes, and Δc is the difference in composition, expressed in mole fraction, (Figure 2).

Zeldovich analyzed the problem of a miscible “interface” in 1949 and concluded that indeed a transient interfacial tension would exist.⁶

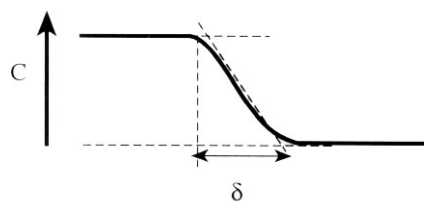


Figure 2. A schematic of an interface between miscible fluids.

Rousar and Nauman demonstrated that assuming a linear concentration gradient the surface tension can be found **without** assuming the system is at equilibrium.⁷ They demonstrated analytically that across a linear concentration gradient, there is a difference between the pressure normal to the “interface” and pressure tangential to it:

$$p_N - p_T = k \left(\frac{dc}{dx} \right)^2 \quad (4)$$

If we integrate across the interface we calculate:

$$\sigma = \int k \left(\frac{dc}{dx} \right)^2 dx \quad (5)$$

Estimation of the Square Gradient Parameter

We estimate the value of k by using thermodynamic theory for polymer in a solvent and by spinning drop tensiometry. Balsara and Nauman derived a relationship:⁸

$$k = \frac{R_{gyr}^2 RT}{6V_{molar}} \left[X + \frac{3}{1-C} \right] \quad (6)$$

where R_{gyr} is the radius of gyration of the polymer, X is the Flory-Huggins interaction parameter. When multiplied by RT it provides the enthalpy of mixing between polymer and solvent. For a good solvent, it is 0.45. V_{molar} is the molar volume of the solvent, which in our case is the monomer, $2.7 \times 10^{-4} \text{ m}^3 \text{ mole}^{-1}$. We do not know R_{gyr} for poly(dodecyl acrylate) but we can obtain an upper estimate from literature results. For polystyrene in toluene at 60°C , $R_g^2 = 9 \times 10^{-16} \text{ m}^2$. Because the concentration across the transition zone varies from 0 to 1, we average the expression up to $C = 0.99$ to obtain at 100°C ,

$$k = 5 \times 10^{-8} \text{ N}$$

The value of the radius of gyration was for high molecular polystyrene (10^6) but the polymer in TIPMPS will be lower. So if we assume an $R_g = 3 \times 10^{-9} \text{ m}$, k could be two orders of magnitude smaller.

It is important to note that this theory predicts that k increases with temperature.

Spinning Drop Tensiometry

The interfacial tension between two fluids can be measured using spinning drop tensiometry, which was developed by B. Vonnegut.⁹ The principle is simple: The more dense fluid is placed into a capillary that is rotated at $> 5,000 \text{ rpm}$ (Figure 3). A drop of the less dense fluid is injected into the capillary. The drop is subject to a pressure jump across the interface, which stretches the drop along the axis of rotation. If this were the only force, the drop would extend until it reached the ends of the capillary and form a column of

fluid inside the more dense phase. Because the volume of the drop is fixed, as the drop stretches, its area increases. Thus the free energy of the surface increases. The longer the drop and the smaller the radius, the lower is the rotational energy but necessarily the surface area is greater. Thus the equilibrium drop radius can be found by finding the minimum energy as a function of radius.

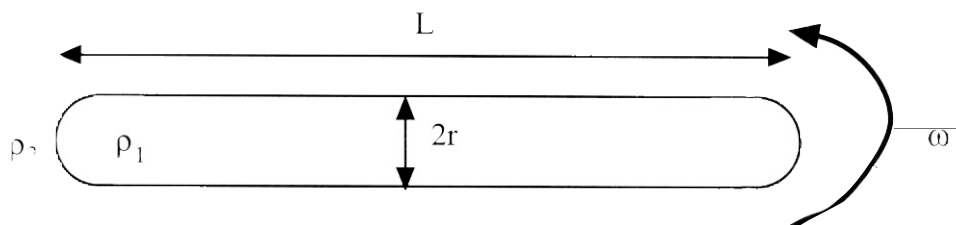


Figure 3. Schematic of a spinning drop

For $L \gg r$, we have the simple relationship:

$$\sigma = \frac{\Delta\rho\omega^2 r^3}{4} \quad (7)$$

Petitjeans measured the EIT for glycerin/water and found that the drop diameter reached a quasi-steady value after 100 seconds.¹⁰ He obtained a value at room temperature of 0.6 mN/m.

We studied dodecyl acrylate in poly(dodecyl acrylate), which we prepared by photopolymerization. We adjusted the molecular weight, and thus the viscosity, by adding dodecyl mercaptan, a chain transfer agent. We prepared it so the viscosity was about 0.1 Pa s at room temperature, the viscosity we will use at 100 °C in the flight experiment.

The densities of the polymer and monomer were measured with a Paar densitometer. A dye, zinc meso-tetraphenylporphine, was added to the monomer. A diode laser sheet was used to illuminate the drop, which was imaged orthogonally. Digital images were analyzed with NIH Image. The drop diameter was defined as the regions in which the spatial derivative of the gray scale was non-zero.

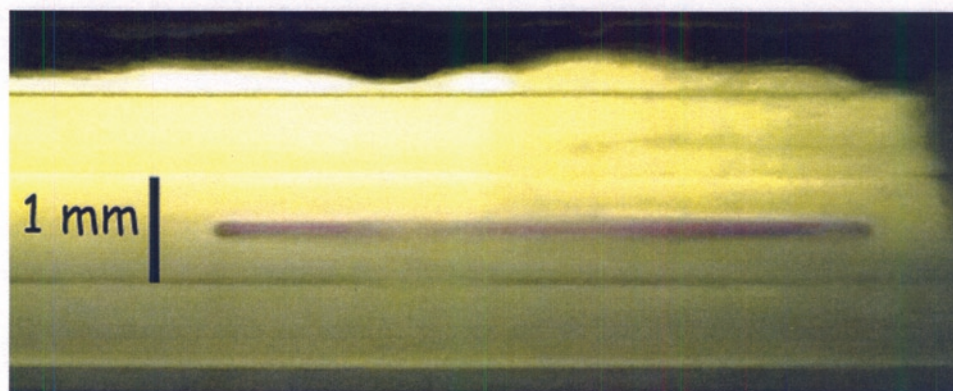


Figure 4. A drop of monomer with dye in poly(dodecyl acrylate) at 25 °C and a rotation rate of 5,000 rpm

Figure 4 shows a drop of monomer after it has mechanically relaxed, a process that requires about 100 seconds. Figure 5 shows that after the mechanical relaxation, the drop radius reaches a quasi-steady value. Hu and Joseph showed that the apparent interfacial tension for immiscible fluids increased with

rotation rate until reaching an asymptotic value at rotations exceeding 6,000 rpm.¹¹ We observed similar behavior for our miscible system with an asymptotic value of 0.08 mN/m for interfacial tension.

Note that in Figure 5 the interfacial tension appears to increase after 1000 s. In fact, it is the radius of the drop but not EIT that increases with time. This can happen if diffusion will have a greater impact on decreasing the density difference than on EIT. Thus, measurements with SDT of EIT in systems with large diffusion coefficients can be complicated because of this dual action of diffusion. The apparent faster rate of growth with time for higher rotation rates is an artifact of the ω^2 dependence of the interfacial tension. In fact, the radius grows at about the same rate for all drops.

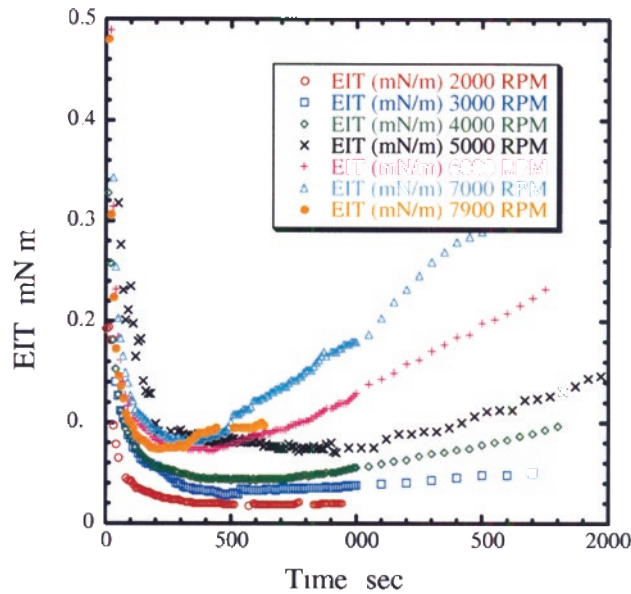


Figure 5. The dependence of the apparent effective interfacial tension on the rotation rate and time.

We estimated the width of the transition zone, δ , to be 10^{-4} m, which yields a value of $k = 10^{-8}$ N. In a previous work,⁵ we explained how we estimated the square gradient parameter from dodecyl acrylate/poly(dodecyl acrylate) and for glycerin/water using spinning drop tensiometry.⁵

Numerical Modeling

We have developed a mathematical model for Korteweg stresses in miscible fluids in which the stress tensor terms are added to the incompressible Navier-Stokes equation. To study the influence of the effective interfacial tension on a monomer and its miscible polymer we consider mass, energy and momentum conservation. If we assume:

- a) Thermal and diffusive fluxes are small,
- b) The internal energy has the form,

$$e = e_0 + k |\nabla c|^2 \quad (8)$$

- c) capillary forces are tangential to the composition gradient,
- d) the fluids are incompressible and have the same density and viscosity, we obtain the following model.

$$\begin{aligned}
\frac{\partial T}{\partial t} + \mathbf{v} \nabla T &= \kappa \Delta T \\
\frac{\partial c}{\partial t} + \mathbf{v} \nabla c &= D \Delta c \\
\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \nabla) \mathbf{v} &= -\frac{1}{\rho} \nabla p + \nu \Delta \mathbf{v} + \frac{1}{\rho} \left\{ \begin{aligned} &\frac{\partial K_{11}}{\partial x_1} + \frac{\partial K_{12}}{\partial x_2} \\ &\frac{\partial K_{21}}{\partial x_1} + \frac{\partial K_{22}}{\partial x_2} \end{aligned} \right\} \\
\text{div } \mathbf{v} &= 0
\end{aligned} \tag{9-12}$$

Where T is the temperature, $\mathbf{v}$ is the fluid velocity, p is the pressure, ν is the kinematic viscosity, ρ is the density and c is the concentration (mole fraction) of polymer. K_{ii} are the stress tensor terms, defined by:

$$\begin{aligned}
K_{11} &= k \left(\frac{\partial c}{\partial x_2} \right)^2 \\
K_{12} = K_{21} &= -k \frac{\partial c}{\partial x_1} \frac{\partial c}{\partial x_2} \\
K_{22} &= k \left(\frac{\partial c}{\partial x_1} \right)^2
\end{aligned} \tag{13-15}$$

where k is system specific, with units of N.

Simulation of Three Cases

We previously validated the model by comparing steady-state simulations, in which the concentration field was fixed, to steady-state simulations of a true interface model.⁵ We have demonstrated that drops of miscible fluids can spontaneously become spherical and that streams can exhibit a Rayleigh-like instability.¹² This model used a fixed grid, constant viscosity with the vorticity-stream function formulation.

We applied another numerical method with the conservation laws (mass, momentum, energy) in integral form (not in differential form) that allows us to introduce a viscosity that is dependent on the concentration.¹³ Instead of the “stream-function and vorticity” we used “pressure-velocity” as the basic variables. We used nonorthogonal Eulerian or Lagrangian meshes. Figure 6 shows the simulation domain. The dependence for the viscosity on the conversion was taken as $\nu(c) = \nu_0 e^{\lambda c}$, with $\lambda = 3, 4$ or 5 .

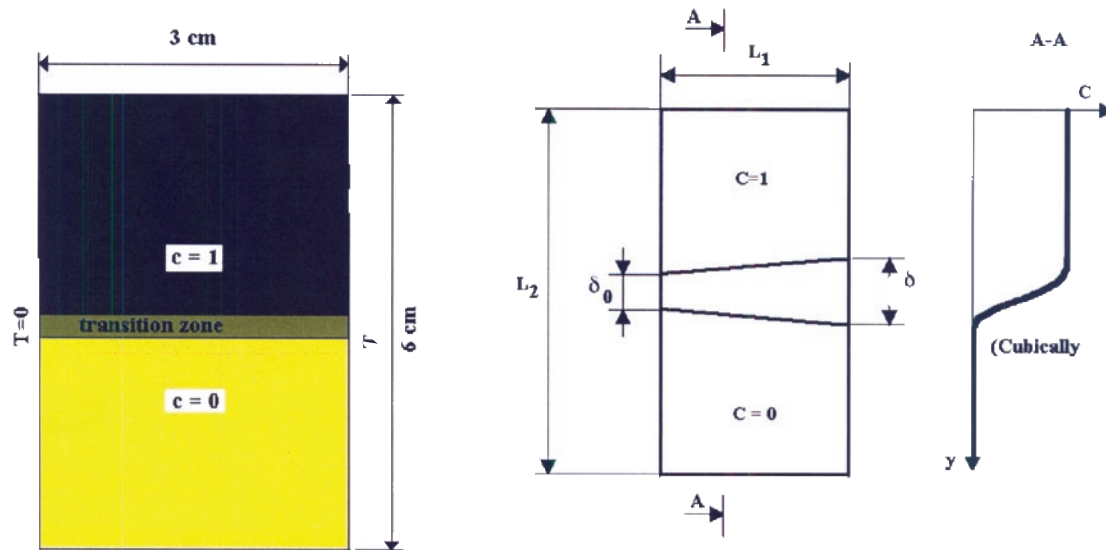


Figure 6. Left: Schematic of the simulation domain. Right: The configuration of the simulations with the variation in the width of the transition zone.

1. Variation in the transition zone.

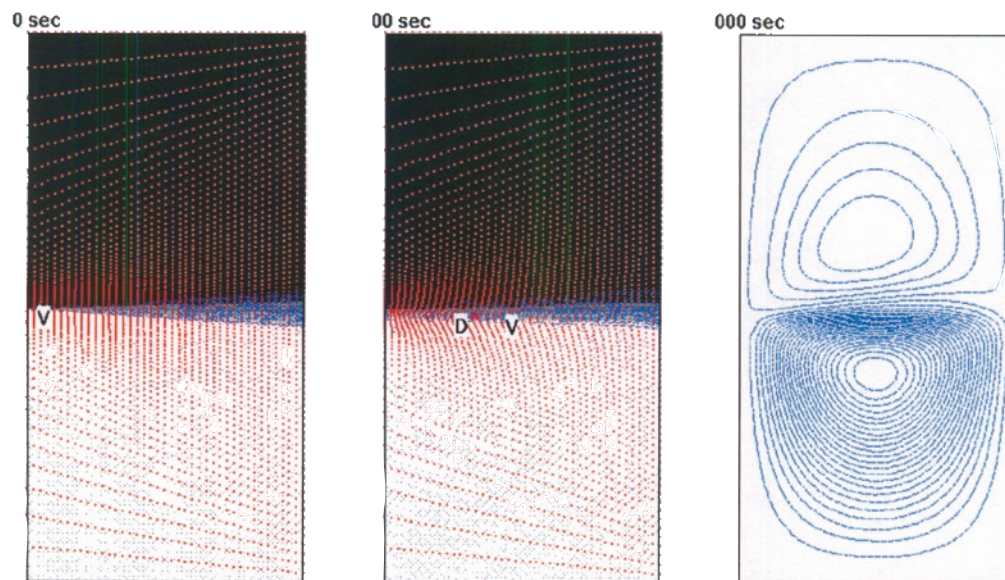


Figure 7. Simulation with a variable transition zone: δ from 0.2 mm to 5 mm with $k = 2 \times 10^{-9}$ N. Polymer concentration is indicated by the gray level.

Figure 6 shows how the transition zone can either be constant or depend on position. If we impose an initial variation on the transition zone, significant flows can occur. Figure 7 shows the fluid displacement and the streamlines after 1000 seconds. Figure 8 demonstrates how the flow increases with the value of k and with the variation in δ but not indefinitely. A variation of 0.2 mm to 5 mm appears to be optimal.

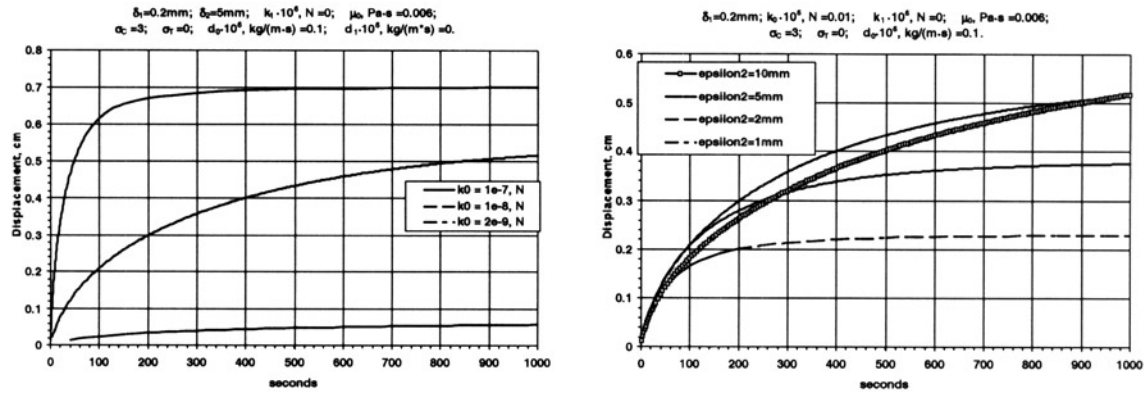


Figure 8. Left: The maximum displacement of fluid as a function of time for different values of k . Right: The maximum displacement for different values of the transition width variance.

2. Effect of Temperature Gradients

We modeled a uniform concentration gradient (constant δ) with a linear temperature gradient parallel to the interface. We studied many cases but we discuss two here. First, we used eq. 6 to estimate the temperature-dependence of k . Figure 9 shows that with a 50 K temperature variation along the transition zone, the induced flow would be extremely weak. However, we estimate that such a change in T would increase the diffusion coefficient four times. When we include that effect with a k that is constant, a significant flow is induced (Figure 9). This occurs because the gradient in the diffusion coefficient creates a gradient in δ .

3. Variation of concentration

The final case is with a constant transition width, no applied temperature gradient but with a gradient in the polymer conversion. The polymer conversion and temperature are linked because complete conversion increases the temperature by 150 K. Figure 10 shows how a significant flow develops. If we include the temperature-dependence of D , then competing effects produce two flows. Although the total fluid displacement can be rather small, the distortion to the concentration field should be readily measurable using optical techniques.

Conclusions

We performed simulations based on Korteweg stresses using parameters for the TIPMPS flight investigation. Convection could be caused by temperature gradients or concentration gradients parallel to the large gradient between the miscible fluids. A variation in the width of this transition also caused convection.

Interesting effects occur if the diffusion coefficient is also temperature dependent.

Our next steps are to include the photopolymerization chemistry and to extend the model to three dimensions.

This work was supported by the NASA (NAG8-1466).

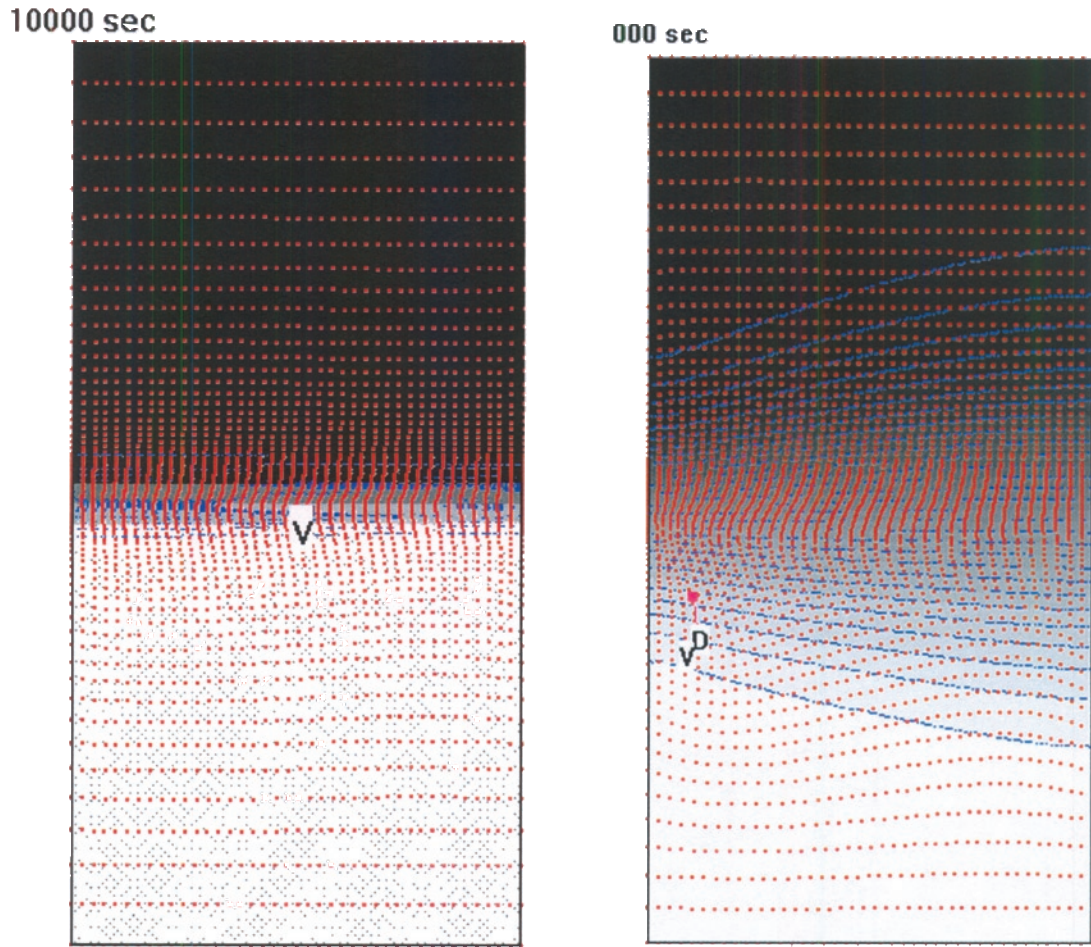


Figure 9. Left: The effect of a variation in k from $1.5 \cdot 10^{-9}$ N to $1.7 \cdot 10^{-9}$ N with μ 0.002 Pa s increasing to 0.3 Pa s, after 10,000 s. Right: With k independent of T , $k = 10^{-9}$ N but the diffusion coefficient increasing four times from right to left, after 1000 s.

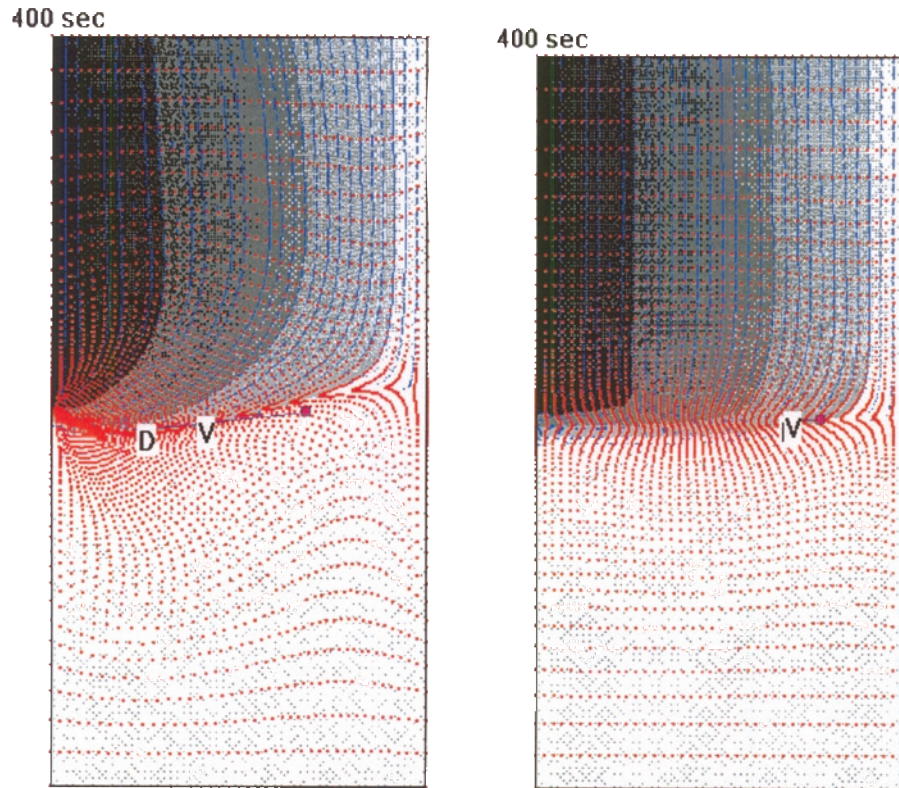


Figure 10. A gradient in polymer conversion along the transition zone with $k = 10^{-8}$ N, $T = 150$ °C for full polymer conversion and $T = 25$ °C. Left: Diffusion coefficient is independent of T . Right: Diffusion coefficient increases with conversion.

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THE EFFECT OF NANOPARTICLES FILLERS ON DEWETTING DYNAMICS

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Nanoscale metallic particles have been added to polymers for years to significantly enhance various properties such as UV absorption, electrical conductivity, and optical dispersion. In contrast to bulk fillers, which are added in large quantities in order to reinforce structural properties, the concentration of metallic nanoparticles required to affect the electronic response is often less than 5%. Furthermore, since these nanoparticles are coated with surfactants used as dispersants, it has been assumed that they do not interact with the polymer chains, and hence do not affect properties such as viscosity, glass transition, or interfacial tensions. Thus, not much attention has been given to the effect of fillers on thin film stability.

Producing a stable polymer film is a challenge, since dewetting tends to rupture the film. Here, we report on a unique strategy to control the rate of dewetting of thin polymer films by dispersion of various nanoparticle fillers. Specular x-ray reflectivity and TEM are used to profile the distribution of the particles in and out of the plane of the substrate, respectively. Optical microscopy and Lateral force microscopy are used to study the growth rate of holes and position of the particles during the dewetting.

We have carried out systematic dewetting studies of polystyrene (PS) on poly(methyl methacrylate) (PMMA) by adding functionalized fillers like Au and Pd. We show that even in the case where particles are well dispersed, large effects on the stability of the film due to dewetting may be induced by the addition of fillers. The rate of dewetting also depends upon nanoparticle concentration in the film. These results are compared with Molecular Dynamics simulations currently being conducted. As for now, these effects are not theoretically proven, but it is clear that by addition of nanoparticles a combination of equilibrium and kinetic effects can be controlled. Two separate models have been developed to prove the mechanism behind the suppression and expression of the dewetting. The effects presented here promise to be an important means of controlling thin film stability.

Keywords: metallic nanoparticles, film stability, dewetting, new research

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**Principal Investigator.

IMPROVED CRYSTAL QUALITY BY DETACHED SOLIDIFICATION IN MICROGRAVITY

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Summary

Many microgravity directional solidification experiments yielded ingots with portions that grew without contacting the ampoule wall, leading to greatly improved crystallographic perfection. Our long term goals have been:

- To develop a complete understanding of all of the phenomena of detached solidification.
- To make it possible to achieve detached solidification reproducibly.
- To increase crystallographic perfection through detached solidification.

We have three major achievements to report here:

- We obtained a new material balance solution for the Moving Meniscus Model of detached solidification. This solution greatly clarifies the physics as well as the roles of the parameters in the system.
- We achieved detached solidification of InSb growing on earth in BN-coated ampoules.
- We performed an extensive series of experiments on freezing water that showed how to form multiple gas bubbles or tubes on the ampoule wall. However, these did not propagate around the wall and lead to fully detached solidification unless the ampoule wall was extremely rough and non-wetted.

Material Balance Solution To The Moving Meniscus Model

Many directional solidification experiments in space yielded ingots with sections that had little or no contact with the ampoule wall [reviewed in 1]. We call this “detached solidification.” When detachment occurs, the dislocation density is greatly reduced and grains and twins can no longer nucleate at the ampoule wall. Regel and Wilcox [2] proposed the Moving Meniscus Model shown in Fig. 1 to explain this puzzling phenomenon. There is a gap between the solid and the ampoule wall, while the melt remains in contact with the ampoule. During solidification, the meniscus moves along the ampoule wall at the freezing rate. There must be a pressure difference across the meniscus because of its curvature. This pressure difference is provided by a gas, which is dissolved in the melt at its top surface, rejected by the growing solid, and released across the meniscus into the gap. Based on the Moving Meniscus Model, numerical calculations were performed for InSb [3-6] and for water [7]. Detached solidification was predicted to occur in a sealed ampoule at zero gravity under proper conditions; the gas pressure P_m above the melt must be above a critical value [3,7], the freezing rate V_c must exceed a critical value [3,7], Henry’s constant H of the dissolved gas must be below a critical value [7], the temperature of the top of the melt must be below a critical value [7], the contact angle θ of the melt on the ampoule wall and the growth angle α must exceed critical values [4], and the diffusion coefficient D of the gas in the melt must exceed a critical value [3,7]. Each critical value depends on the other physical properties and operating conditions, so that different results were obtained for InSb and water

Keywords: indium antimonide, detached solidification, dewetting

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[7]. Within the range of parameters predicted to yield steady-state detachment, two solutions were found, one with a large gap and one with a small gap between the solid and the ampoule wall.

As is typical of numerical simulations, a thorough understanding of the factors contributing to the behavior predicted above has been elusive. For that reason we sought to develop an approximate analytical solution. We were encouraged by the observation that although Marangoni convection along the meniscus dramatically alters the velocity and concentration fields, it does not markedly influence detachment [3]. A steady state material balance approach was successful, and does reveal the essential physics [8].

Non-dimensionalization of the governing equations for the Moving Meniscus Model allowed consolidation of the operating conditions and physical properties into five dimensionless parameters. At steady state, the flux of gas dissolved in the melt moving toward the freezing interface must equal the sum of the flux of gas into the gap plus that being incorporated in the growing solid. Both numerical and material balance results give two solutions, with an extremum value of each variable beyond which steady detachment is impossible. This behavior is now understood to originate from satisfaction of the material balance at two different gap widths, with these two solutions becoming identical at an extremum condition beyond which the material balance cannot be satisfied. Only one solution is obtained when no gas is incorporated in the solid. In the presence of gravity, the gas pressure in the gap must be much larger to compensate for the added hydrostatic pressure, causing the gap width to be narrow.

Figure 2 shows the material balance volume used to obtain an approximate analytical solution for steady state detached solidification. The flux N_L of dissolved gas into this volume was found from the freezing rate and the concentration of dissolved gas, which was assumed to be the solubility of residual gas in the melt at the temperature and pressure at the top of the melt. The flux N_G of gas into the gap was obtained from the pressure of gas inside the gap, which was calculated from the curvature of the meniscus, the curvature of the top surface of the melt, and the hydrostatic head (on earth) of the column of melt. The flux N_s was obtained from the equilibrium distribution coefficient of dissolved gas in the solid together with the dissolved gas concentration in the melt along the freezing interface. The concentration field was obtained by an approximate analytical solution of the partial differential equation for diffusion. At steady state, the flux into the volume must equal that out, or $N_L = N_s + N_G$.

Figure 3 shows the three fluxes versus the gap width for a base set of values of the governing parameters. For these conditions, there are two steady state solutions where the curve for $N_s + N_G$ intersects that for N_L . By varying the experimental parameters, the curve for $N_s + N_G$ can be raised so that the two solutions become closer and closer. When the two curves become tangent, there is only one solution. As $N_s + N_G$ is raised still farther, the two curves do not intersect and steady state detachment is impossible.

The computer algebra system Maple was used to find the gap width e versus various parameters. Figure 4 shows a comparison of results predicted from this material balance method to those predicted from numerical solution of the differential equations for the Moving Meniscus Model. At small values of the gap width the agreement is excellent, but the two methods diverge somewhat for large values of the gap width. This reflects the error in the estimate of the dissolved gas concentration along the freezing interface. Nevertheless, both methods show maxima in the values of the parameters that will yield a solution. Figure 4 also confirms the utility of non-dimensionalizing the governing equations, as well as indicating the error in the numerical solution.

The influence of gravity was also investigated. The added hydrostatic pressure in the gap causes the steady state gap widths to become smaller. Furthermore, detachment is not possible unless the segregation coefficient k is small. Convection was not considered here, but may either increase or decrease the flux of gas into the gap, depending on the convection pattern and its vigor [6].

Detached Solidification Of InSb On Earth

Indium antimonide (InSb) has often exhibited detached solidification from microgravity experiments. Here, we directionally solidified InSb on earth using the vertical Bridgman-Stockbarger technique [10]. A pyrolytic boron nitride (BN) coating was formed on the inside of some of the quartz ampoules by reacting a layer of boric acid with ammonia gas. Detachment often occurred, as illustrated in Figures 5, 6 and 7. It was favored by the boron nitride coating, a 10 mm/h growth rate, and 20 kPa of forming gas (10% H₂ in Ar) in the ampoule. The detached portion sometimes completely circled the ingot, and sometimes went only part way around. Tiny facets could be seen on many detached regions. Detachment did not occur at the top or bottom of the ingot, when the ampoule was too short, or when the ingot was oxidized due a leak in the ampoule.

Gas Bubble And Tube Formation In Ice

A vertical Bridgman-Stockbarger apparatus was used to directionally solidify water upward, in the hope that detached solidification would evolve from gas bubbles forming on the wall [9,11]. A large contact angle of the water on the ampoule wall and a high solubility of the dissolved gas caused gas bubbles or tubes to form only at the ampoule wall, and not in the interior. Gas tubes were often nearly periodically spaced around the ampoule wall (e.g., Figure 8), with a spacing that increased with ampoule diameter and decreased with freezing rate. The width of the gas tubes was nearly independent of the ampoule diameter and freezing rate. A high degree of detachment was obtained with a rough, non-wetting coating on the ampoule wall, but full detachment was not achieved. This indicates that detachment does not occur by propagation of a single gas bubble around the periphery of the freezing interface. The convection near the freezing interface influenced gas bubble formation, and was outward for a concave freezing interface and inward for a convex interface.

Similar semi-periodic gas tubes were produced in freezing of zone-refined naphthalene [12].

Acknowledgement

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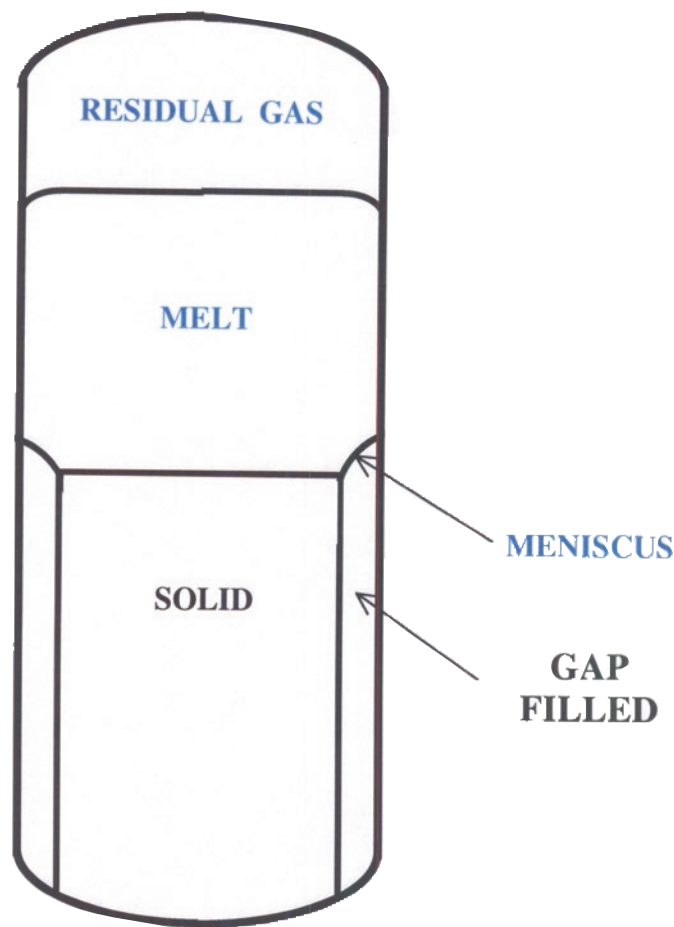


Figure 1. Schematic diagram of the Moving Meniscus Model for Detached Solidification.

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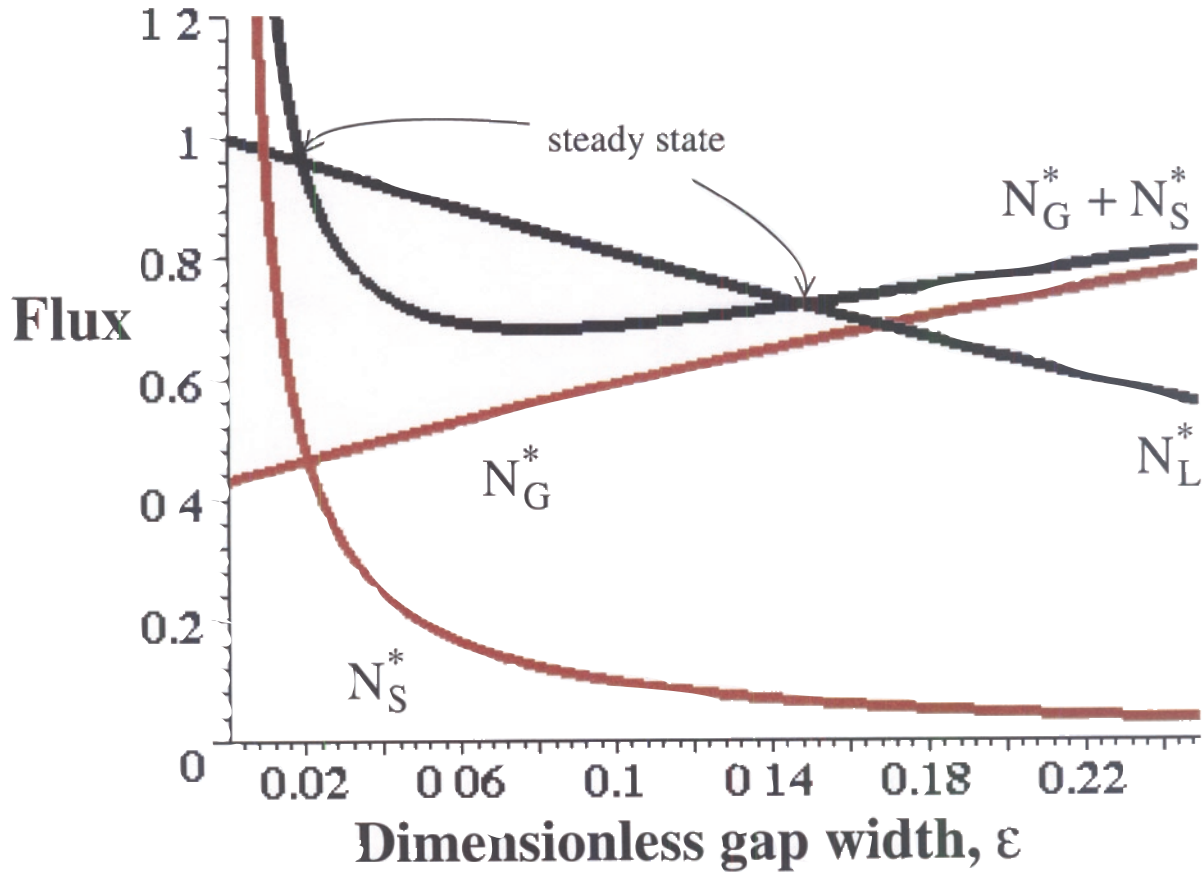


Figure 3. Dimensionless fluxes of dissolved gas versus gap width for base conditions at zero gravity. The fluxes were non-dimensionalized by dividing by the flux of dissolved gas coming in with the melt when there is no gap. The gap width e was non-dimensionalized by dividing by the ampoule radius. For the conditions used to calculate the results shown above, there are two steady state solutions where the curve for $N_s + N_G$ intersects that for N_L . By varying the experimental parameters, the curve for $N_s + N_G$ can be raised so that the two solutions become closer and closer. When the two curves become tangent, there is only one solution. As $N_s + N_G$ is raised still farther, the two curves do not intersect and steady state detachment is impossible.

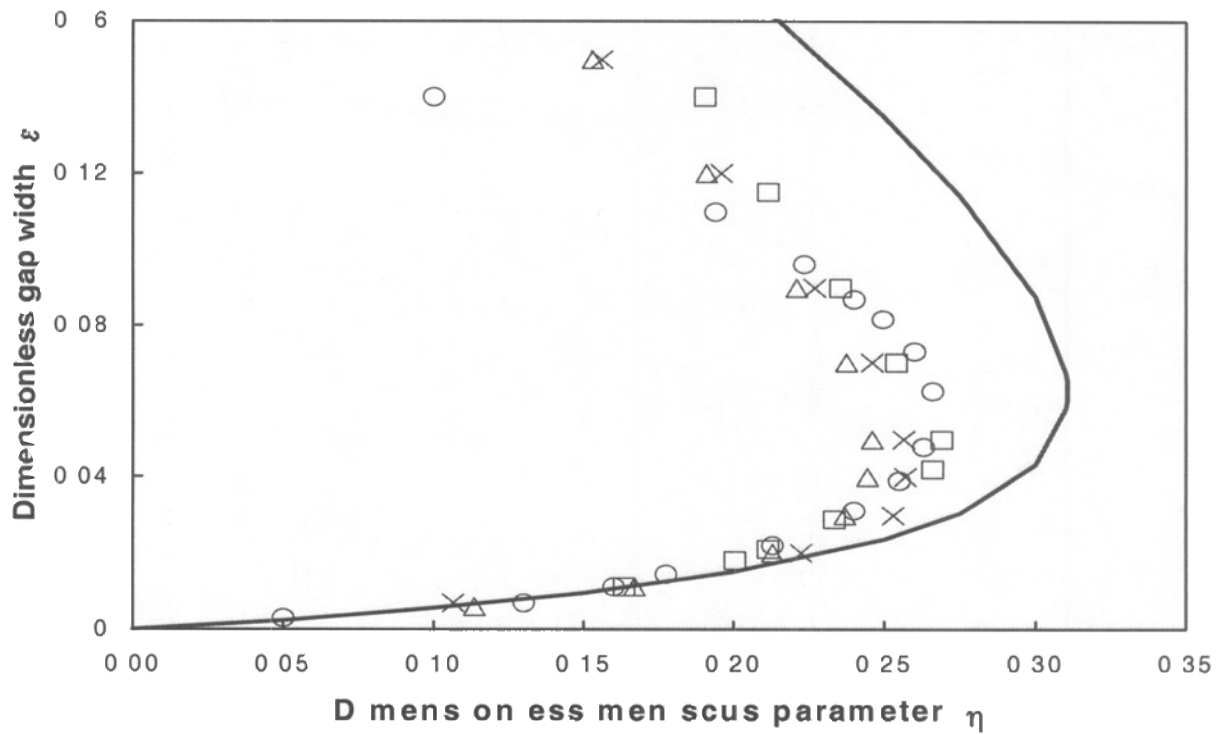


Figure 4. Comparison of the material balance solution with results from numerical solutions of the Moving Meniscus Model for the limiting case of very large ampoule with different parameters held constant.

- x Numerical for σ varied
 □ Numerical for P_m varied
 ○ Numerical for η varied
 △ Numerical for θ varied
 — Material balance

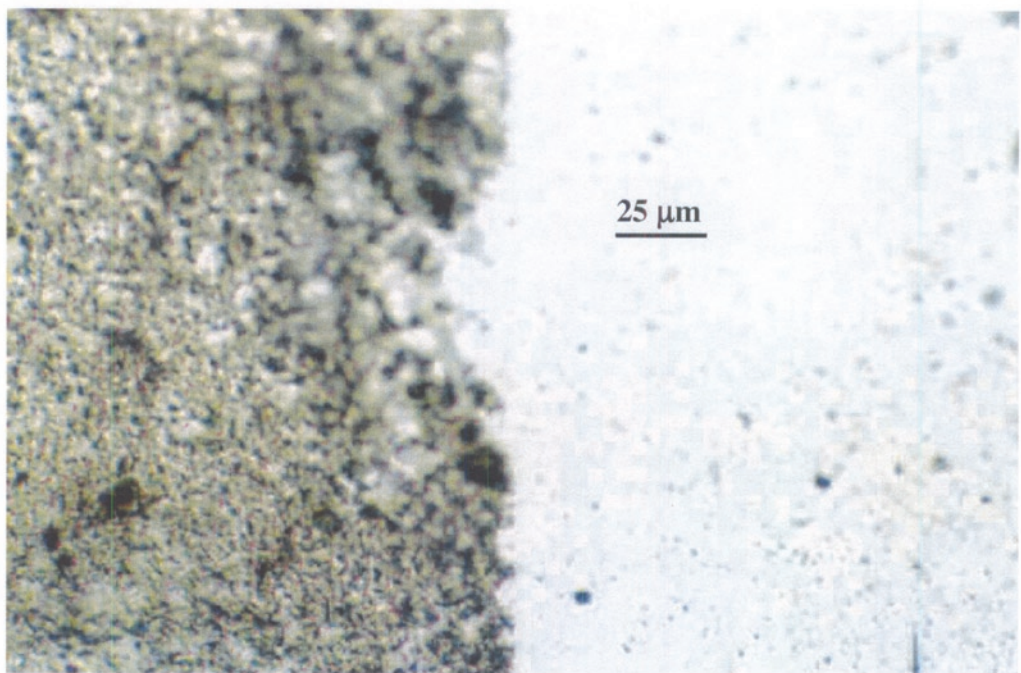


Figure 5. Close-up of boundary between detached and detached sections of ingot 6. Taken at 400 X.

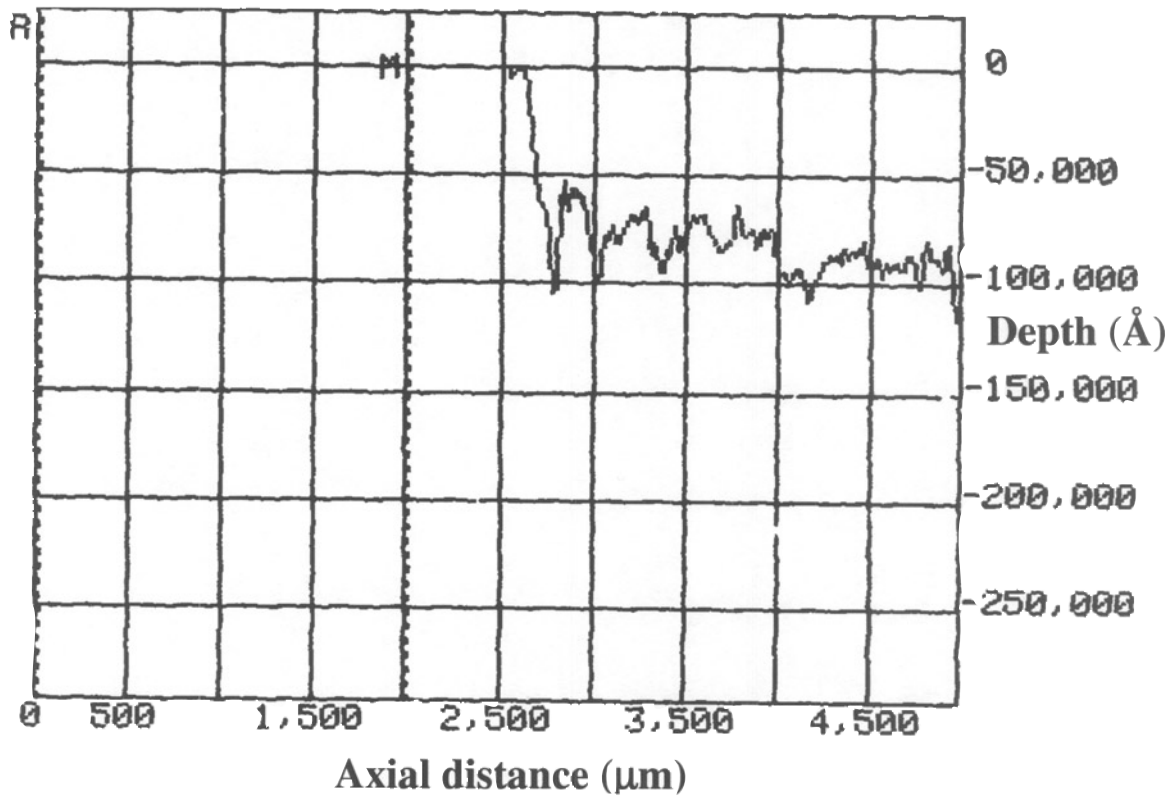


Figure 6. Topography of ingot 6 via profilometer scan lengthwise along the surface.

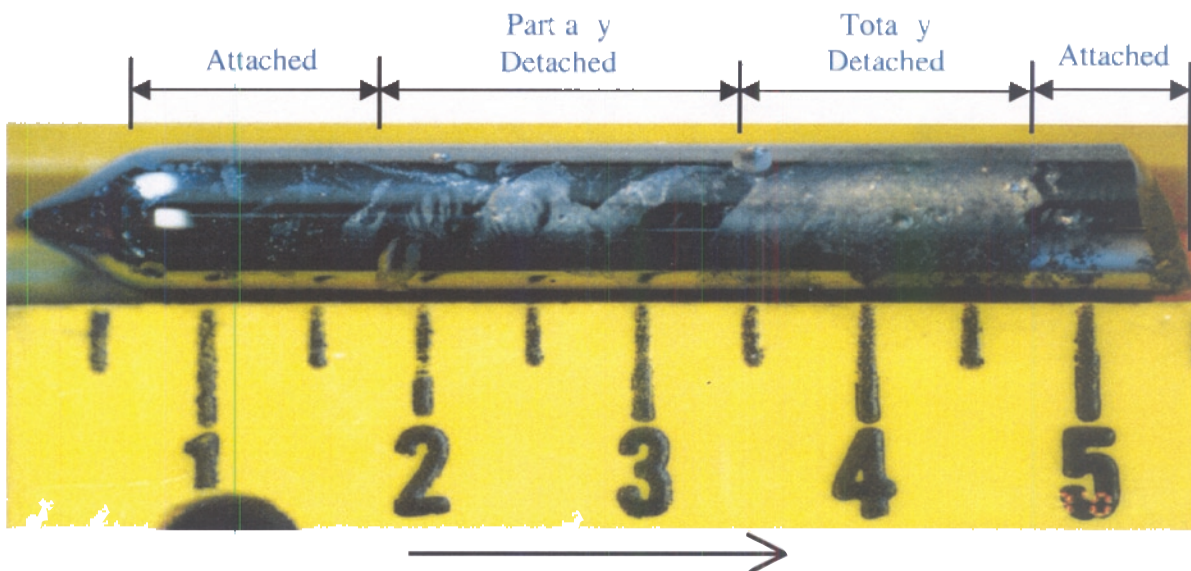


Figure 7. Photograph of Ingot 6. Scale is in cm. The arrow indicates the growth direction.

Growth conditions are: BN-coated ampoule, 10 mm/h freezing rate, 50 kPa of forming gas inside the growth ampoule. “Totally Detached” indicates that the entire circumference grew without contacting the ampoule, while “Partially Detached” indicates that detachment only went part way around.

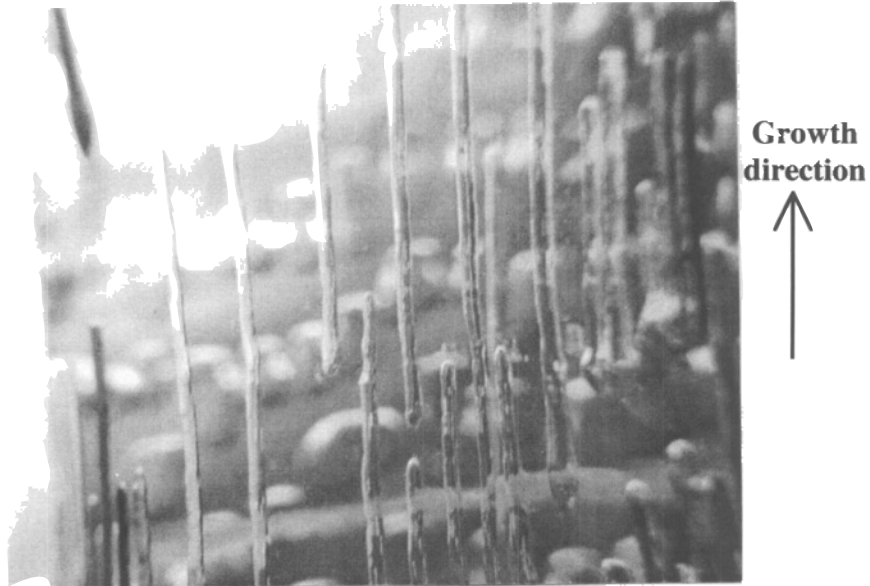


Figure 8. Roughly periodic gas tubes formed on the ampoule wall with a freezing rate of 12 mm/h. The water was saturated with air and the 10 mm inside diameter ampoule was coated with Teflon. Sample width ~10 mm

MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF MOLTEN SILICON AND GERMANIUM

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Introduction

As demands for larger and higher quality semiconductor crystals increase, it has become very important for crystal growers to understand and to control the formation kinetics of a variety of defects such as point defects, non-uniform distribution of doping atoms, and impurity atoms in the growing crystals. However, in a crystal growth environment where accurate thermophysical properties are lacking, it is difficult to expect reliable results from modeling efforts. Importance of accurate thermophysical properties for crystal growth cannot be overly emphasized. The total hemispherical emissivity of a melt, for instance, has a dramatic impact on the thermal environment. It determines radiative emission from the surface of melts, which, in turn determines to a large extent the profile of solidified crystals. In order to understand convection and turbulence in a melt, knowledge on accurate liquid viscosity is important. Liquid surface tension is also important since it determines the shape of the liquid-atmosphere interface near the solid-liquid-atmosphere triple point.

Over the last ten years, there have been several projects, which were organized to measure accurate thermophysical properties of molten silicon using various techniques [1-15]. However, the thermophysical properties measured by these projects showed wide scatter, thus failing to show a converging trend. A possible reason for this scatter might be due to the gravity field present in the ground base experiments, which might have directly or indirectly, affected the property measurements. Another possible reason might be in the containers that have been used. When a certain container is used to measure properties of a melt, the measured properties of the melt tend to show strong crucible dependence. The reasons are both physical and chemical in nature. Molten silicon and germanium are highly reactive with most crucibles. If a certain chemical reaction takes place during a property measurement process, one cannot avoid the effects of contamination on the experimental results. The conventional oscillating cup method for viscosity measurement relies on the wetting properties of melt with crucible. If there were physical slip taking place at the interface, the resulting viscosity would be erroneous. Containerless approach alleviates the problems, which are chemical in nature, by isolating melts from containers. However, levitation experiment conducted in the strong gravitational field also suffers from different kinds of problems, which are physical in nature. Molten silicon and germanium are low viscosity liquids that are in the range of 1 mPa·s. Such low viscosity liquids are susceptible to external forces such as gravity as well as the levitation forces. In the presence of density differences, gravity causes convective flow in the melt affecting the transport properties in particular. Strong perturbing forces that are generated by the levitation forces, tend to generate additional internal flows as well as various instabilities in the drop, increasing the uncertainties in the measurement results. These problems may be greatly reduced by conducting experiments in the

Keywords: molten silicon, germanium, ESL, thermophysical properties, characterization

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micro-g environment where density driven convection is absent and the perturbation forces originating from the sample levitation can be reduced by several orders of magnitude.

Program Objectives

The main objective of this program is in measuring thermophysical properties of molten silicon, germanium, and Si-Ge alloys in the ground base using an electrostatic levitator (ESL) and in identifying areas where the gravity plays limiting roles in measured properties. With limiting areas well identified it is hoped to conduct property measurements in the extended microgravity environment that will be provided by the International Space Station (ISS).

Thermophysical properties that will be measured will include:

- (i) Density,
- (ii) Thermal expansion coefficient,
- (iii) Surface tension,
- (iv) Viscosity,
- (v) Specific Heat/Hemispherical total emissivity,
- (vi) Electrical conductivity.
- (vii) Thermal Conductivity

All the above properties will be measured as a function of true temperatures. During the flight definition period, the ground base electrostatic levitators (ESL) that are available both at Caltech and MSFC will be used.

Present investigation can be subdivided into the following three successive phases: In the first phase, properties of pure semiconductors will be investigated in a high vacuum. In the second phase, effects of impurity contents on the thermophysical properties of the materials will be investigated. In the third phase, the effect of oxygen on the surface tension and the viscosity will be investigated.

Progress

The electrostatic levitation (ESL) facility that was developed at the Jet Propulsion Laboratory was moved to the Caltech Materials Science Department in April 2001. Since the move the system has been up-graded both in hardware and software so that the facility is easier to operate and properties can be measured more accurately.

PC computers with real time PCI boards have replaced the outdated computers and the old levitation software has been replaced by newly developed software that runs with a high speed (1 kHz) control loop for extremely stable levitation and sample positioning.

The most important improvement was in attaining uniform sample temperature. In the previous experiments levitated sample was heated using only one laser. In the single laser beam heating a large temperature gradient across a sample is unavoidable. Large temperature gradient across the sample meant creation of convection flows in the sample causing inaccuracies in measured transport properties. Thus one of the major upgrades that has been made in the Caltech ESL was to design and implement a four-beam heating system that warrants uniform sample temperature. We have developed, installed, tested, and implemented a high symmetry tetrahedral heating system which provides for heating of spherical samples to elevated temperatures (2000 C and above) using 4 laser beams that are arranged to irradiate

the spherical sample symmetrically on the 4 axis of a tetrahedron. Both the theory and experimental test have shown that this tetrahedral heating system should reduce sample temperature gradients by up to two orders of magnitude compared with single beam heating with a focussed laser beam. At the present, the NASA/Caltech ESL with the tetrahedral sample heating system has the capability of high stability levitation, melting, undercooling, and processing spherical droplets of metal alloys and other materials under *very near isothermal and mechanically quiescent* conditions. The result is the substantial and dramatic reduction in driving forces for externally driven convective flow, gravity driven convective flow and Marangoni convective flows within the sample by comparison with any other available platform for containerless processing of liquids. We have shown that liquids at temperatures up to at least 2500 C can be processed under these “benchmark” quiescent conditions. The facility thus provides a unique platform for carrying out a broad range of containerless processing studies of liquids both on the ground, and potentially in microgravity. The schematic view of the high symmetry tetrahedral heating beams is shown in Fig. 1. The main laser beam was equally split into a set of four parallel beams. Three of the four beams are reflected by mirrors to irradiate the sample that is positioned at the center of the tetrahedron. Fig. 2 shows the overall view of the chamber with optical components arranged for the tetrahedral beam heating. The electrode assembly newly constructed for the tetrahedral heating arrangement is shown in Fig. 3. Shown in Fig. 4 is the control room from which the ESL facility is controlled remotely.

Density of a high temperature melting material is measured by video-imaging levitated sample and analyzing the images for volume changes as the sample temperature is changed. However, the density so obtained will be erroneous if the imaging sensor has blooming effect. An important improvement has been made to reduce such undesirable errors by selecting a sensor that is sensitive to the back lit UV while ignoring the thermal radiation from samples. Also developed was a new image acquisition/analysis software that can acquire images in real time and analyze them for the detection of volume changes.

New temperature measurement/analysis software was developed. Along with independently measured spectral emissivity measured by the DOAP, we are ready to measure the true sample temperatures of levitated samples.

Development of a method that can accurately measure surface tension and viscosity is in progress. This method utilizes a line scan video camera to detect both the frequencies and the damping constants of oscillating drops. This approach is expected to increase accuracy in measured surface tension and viscosity.

Acknowledgements

The upgrading of the Caltech ESL facility was done in collaboration with Professor William Johnson, the theoretical analysis of tetrahedral heating system was done by Dr. Jan Schroers and Dr. Sven Bossuyt, and the experimental test of the tetrahedral heating system was assisted by Mr. Jianzhong Li and Dr. Zhenhua Zhou.

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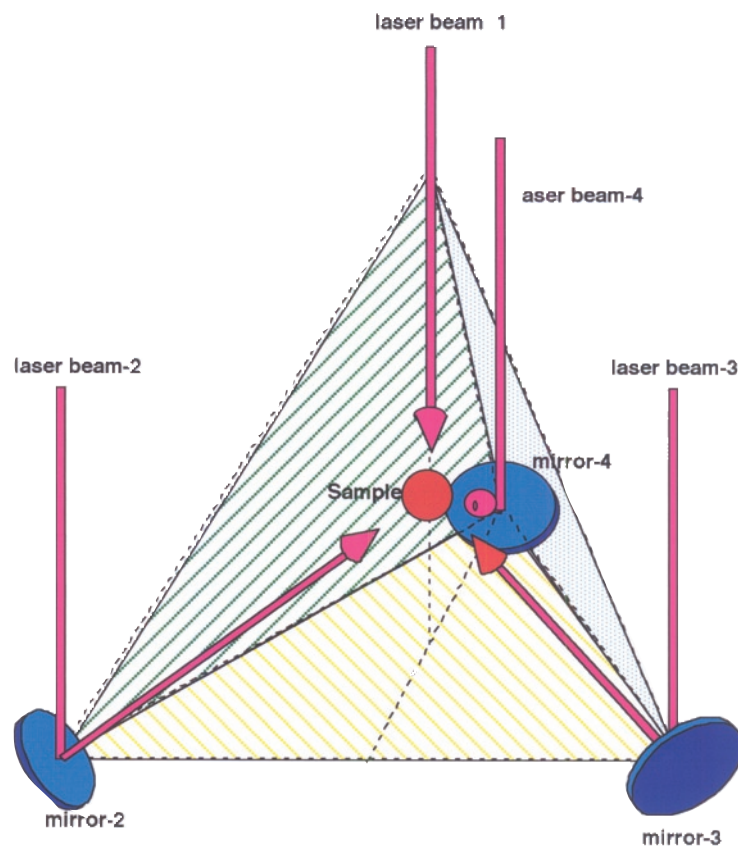


Fig. 1. Schematic view of the high symmetry tetrahedral heating system.

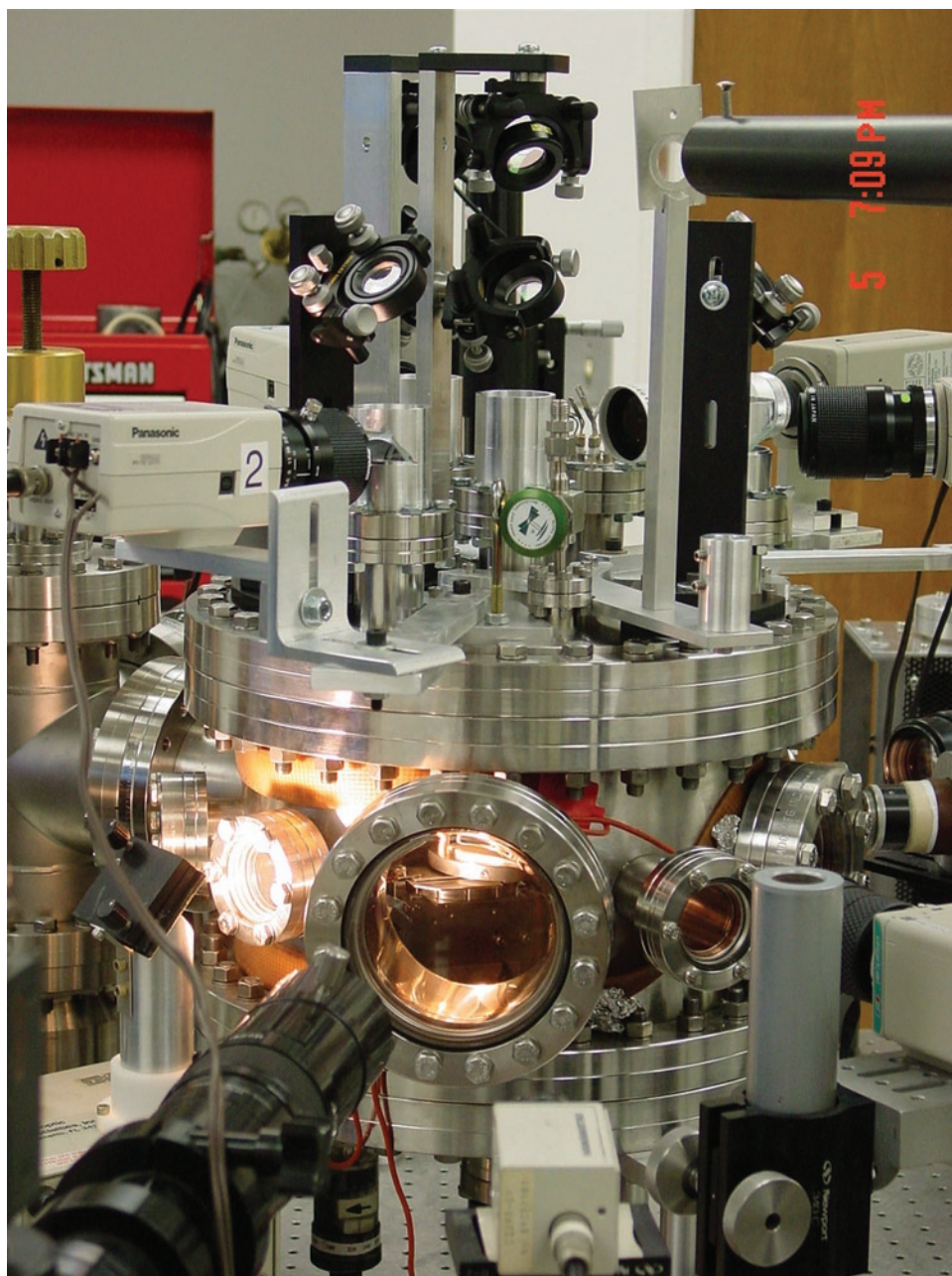


Fig. 2. Overall view of the chamber with optical components arranged for the tetrahedral beam heating.

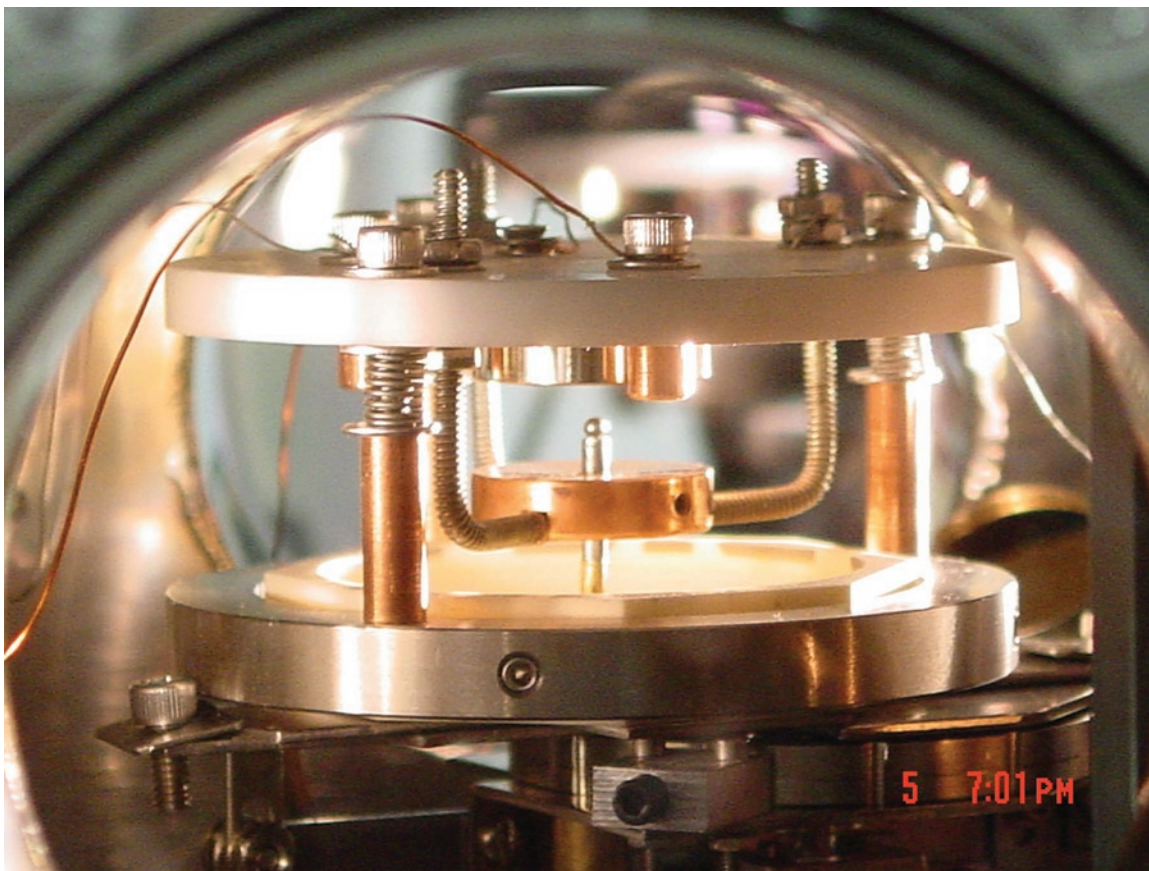


Fig. 3. Electrode assembly newly constructed for the tetrahedral heating system.

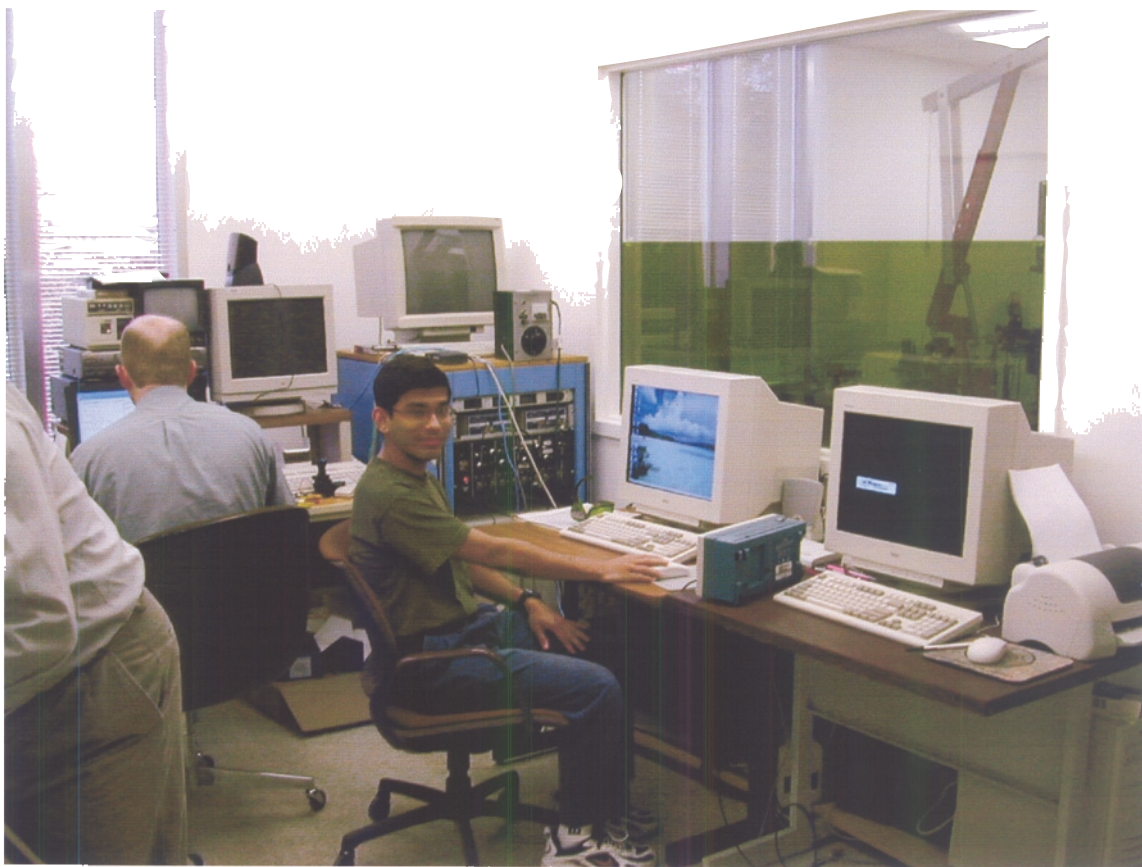


Fig. 4. Caltech ESL facility seen from the control room from which experiments are conducted remotely.

CARBON-BASED REDUCTION OF LUNAR REGOLITH (CRLR)

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Orbital Technologies Corporation (ORBITEC)

ORBITEC has developed a new high-temperature processing technique to produce oxygen and metals from lunar regolith via carbonaceous high-temperature reduction. A CO₂ laser is used to locally heat and process the lunar simulant. The surrounding simulant effectively insulates the container from the high processing temperatures. This technique overcomes problematic issues inherent in traditional high-temperature processing methods that employ crucible-type containment vessels and hot-walled (i.e., resistance or inductive) furnaces. Crucible containment structures either crack from thermal and mechanical stress and/or react with the molten reaction mix, making it very unlikely that such a material could survive the repeated high-temperature thermal cycling in an economical LOX plant on the Moon. The direct heating method will allow extremely high processing temperatures (>2000 C) and eliminate the difficult requirement of developing a containment vessel that withstands these temperatures, is impervious to prolonged chemical attack, and is capable of thermal cycling.

A ground-based experimental system was designed, built, and tested. The experimental system includes an integrated reaction chamber, CO₂ laser equipment, laser beam rastering system, residual gas analyzer, and the control computers. Software was been developed to operate the mass spectrometer, control the laser power, and perform data acquisition on a desktop computer. A second computer is used to control the laser beam rastering system. An internal circulation fan was integrated to keep the zinc selenide laser window in the reaction chamber clean during laser processing. Heat transfer models were developed to predict the temperature gradients in the lunar simulant during laser processing. Thermocouples were also installed in the simulant to directly measure the surface temperature gradients during laser processing.

Carbothermal reduction of the lunar simulant was demonstrated using two different methods. In the first case, carbon black was mixed directly in the lunar simulant. This mixture was placed inside the reaction chamber and laser heated in a pure argon gas environment. Analysis of the product gas showed the formation of carbon monoxide, indicating carbothermal reduction. The second method placed simulant inside the reaction chamber in an argon and methane gas environment. Analysis of the product gas showed the formation of carbon monoxide gas. Hydrogen reduction of the lunar simulant was also demonstrated with the direct heating approach. The experimental results were used to develop a preliminary design of a lunar flight experiment and a pilot production plant.

Keywords: lunar regolith, oxygen production, carbothermal reduction, direct heating

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THE INFLUENCE OF THE NUCLEATION ENERGY BARRIER ON THE MORPHOLOGICAL EVOLUTION AND COARSENING OF FACETED CRYSTALS

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Introduction

The theory for the morphological evolution of crystals bound by rough surfaces is well developed. For example, kinetic laws have been established for capillary driven coarsening^{1,2}, thermal groove development³, surface flattening⁴, scratch healing⁵, and shape changes.^{6,7} A key assumption of these theories is that the surfaces are rough. In other words, atoms can be removed from or added to the crystal without an energy barrier so that shape changes can occur at rates determined either by diffusion or by the kinetics of the surface attachment process. In this paper, we consider the situation where the crystal is bound by singular or nonrough surfaces, which correspond to cusps in the plot of surface free energy as a function of orientation. In this case, facets can move in normal directions only when a step propagates across the surface and adds or removes a layer of atoms. If the facet contains no preexisting steps, then a nucleation event is required to provide a propagating step. The requirement for two-dimensional nucleation creates a so-called “growth resistance” which can only be overcome by either a very high supersaturation^{8,9} or by the presence of a persistent step-generating defect such as a screw dislocation.^{10,11} The purpose of this paper is to demonstrate that this basic difference in the mechanism by which faceted and rough crystals change shape has an important influence on the morphological evolution of crystalline solids.

At the outset, we should recognize that the implications of the nucleation requirement for the morphological evolution of faceted crystals in situations where the driving force is low has been recognized by other researchers. For example, Herring^{12,13} noted that the two-dimensional nucleation barrier would prevent the surface free energy motivated motion of ideal singular facets during sintering. Searcy¹⁴ elaborated on this point and argued that for a fully faceted particle with no dislocations to evolve to a new fully faceted shape closer to equilibrium, it would have to transform through an unfavorable configuration, and that the probability of this happening decreases as the size of the particle increases. Thus, although the potential importance of the nucleation energy barrier (NEB) was recognized by at least some researchers, it was not quantified. As a result, observations of faceted materials have usually been interpreted in terms of kinetic laws appropriate for crystals with rough surfaces, under the assumption that a persistent source of steps is available. This approach is entirely justified, as long as the crystal is large enough (say 10 μm) that the presence of a step creating defect is guaranteed. The interesting point here is that for very small crystals, less than a micron in diameter, the presence of a step-generating defect is far less likely and, in these cases, the NEB makes the kinetic laws for crystals with rough surface inappropriate. Considering the growing importance of materials with nanometer scale dimensions, it is interesting to consider the behavior of faceted materials in this size range more carefully.

Keywords: crystal growth, coarsening, nucleation, faceted crystals, new research

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In the remainder of this paper, the NEB is calculated for several situations and compared to the energy available from thermal fluctuations. The existence of a “kinetically locked” size range is then hypothesized for faceted crystals. This size range extends from a few tens of nanometers to the micron region, depending on the temperature and the crystal’s defect structure. Experimental support for this hypothesis is then described and the paper concludes with a summary.

Driving Force

We consider here changes in crystalline morphology that occur with low driving forces. These include shape evolution, coarsening, and the spheriodization of filamentary or planar structures. Two of these processes are illustrated schematically in Fig. 1. It must be recognized that the driving forces for these processes are very small. For example, the diving forces for capillary driven coarsening are illustrated in Fig. 2. In this example, we have taken the driving force to be $2\sigma\Omega[(1/r^*)-(1/r)]$, where r is the particle radius, r^* is the radius of a particle that neither grows nor shrinks, Ω is the atomic volume, and σ is the surface free energy per unit area. If we assume a typical atomic volume and take r^* to be $1\text{ }\mu\text{m}$ and σ to be 1 J/m^2 , then we can estimate that the energy difference between a particle at r^* and one about 100 times larger is $2\sigma\Omega/r^* = 3 \times 10^{-23}\text{ J}$. In other words, the driving force for growth is several orders of magnitude smaller than the available thermal energy at $1500\text{ }^\circ\text{C}$ ($2 \times 10^{-20}\text{ J}$).

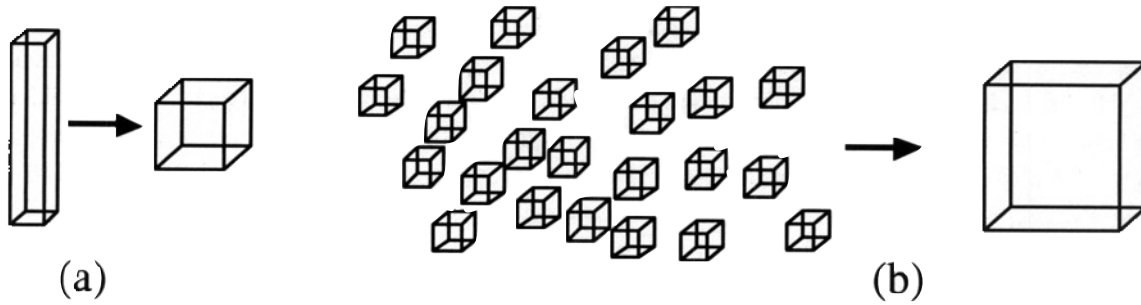


Figure 1. Capillary driven processes with low driving forces. (a) An anisotropic particle evolves to its equilibrium shape and (b) small crystals coarsen to reduce the total surface energy.

Morphological Evolution

There is an extensive literature dealing with capillary driven shape changes in the absence of nucleation and authoritative reviews on the subject already exist.^{15,16} Therefore, we focus on the mechanisms for the shape evolution of faceted crystals.

To quantify the size of the NEB in the simplest possible way, we consider an isolated crystal with its equilibrium cube shape, an edge length of L , and a surface energy of σ , and calculate the energy change as a layer of atoms from the top of the crystal is transferred to the side face, as illustrated in Fig. 3. As material is removed from the top facet, a square island with area s_2^2 and height a is created on the side facet and a square island with area s_1^2 and the same height is left behind on the top facet. Because matter is conserved, $L^2 = s_1^2 + s_2^2$. Obviously, the only energy change in this process is associated with the change in the edge energy and assuming that the step edges have the same energy per area as the facets, σ , then the energy change is:

$$\varepsilon_b^e(s_1) = 4a\sigma s_1 + 4a\sigma s_2 - 4a\sigma L = 4a\sigma(s_1 + \sqrt{L^2 - s_1^2}) - 4a\sigma L \quad (1)$$

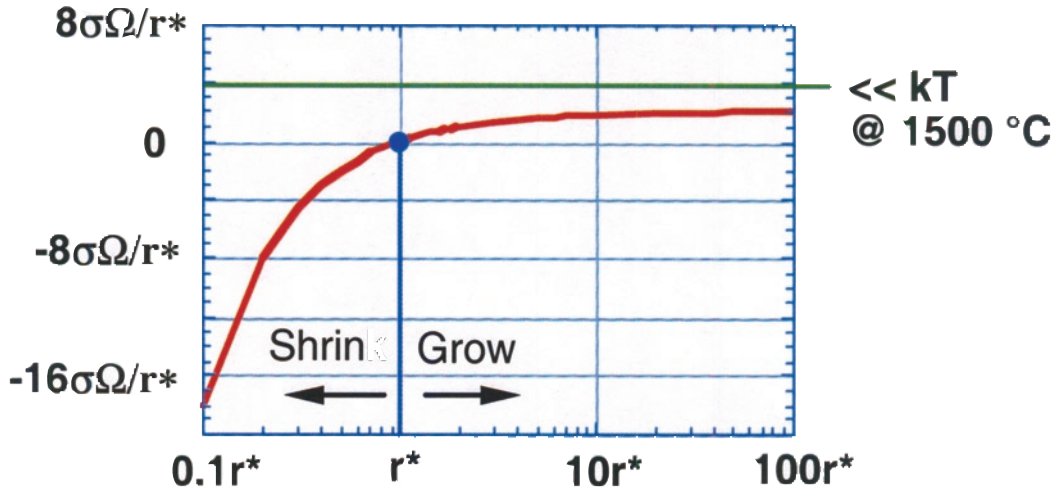


Figure 2. The driving force for capillary driven coarsening, $2\sigma\Omega[(1/r^*)-(1/r)]$, where r is the crystal radius, r^* is the radius of a particle that neither grows nor shrinks, Ω is the atomic volume, and σ is the surface free energy per unit area. For growing crystals, the driving force is a small fraction of the energy available from thermal fluctuations.

In Eq. 1, the first two terms in the middle component of the equation represent the added perimeter energy while the last one represents the energy eliminated. It is clear from Eq. 1 that there is no net energy change to transfer a layer in either direction; this point is illustrated graphically in Fig. 3. Figure 3 also demonstrates that to transfer the layer, the crystal must pass through an intermediate state with a higher energy. The maximum is reached when the area of the partial layer on each facet is the equal ($s_1=s_2=L/\sqrt{2}$). If we return these numbers to Eq. 1, we see that the barrier to the transfer of a layer from one facet to another is $1.66 a\sigma L$.

It has been shown that nucleation on a facet can be considered negligible if the barrier energy is $\geq 40kT$.¹⁷ This estimate is based on a classical expression for the steady-state nucleation rate on an infinite singular facet and defines nucleation rates $\leq 10^{-4}\text{nm}^{-2}\text{s}^{-1}$, equivalent to a rate of less than one atomic layer per hour on a facet of 1nm^2 , as negligible.¹⁸ If we take a to be $3\text{\AA}$, σ to be 1J/m^2 , and $T=1000\text{ }^\circ\text{C}$, then the barrier will only be surmounted for particles where $L \sim 1.4\text{ nm}$. In other words, for defect free particles of sizes greater than a few nm, the NEB will prevent fluctuations about the equilibrium shape. While the argument above considers only the case for a crystal already in its equilibrium shape, where there is no driving force for a change in shape, the same reasoning has been extended to nonequilibrium shapes and similar results are obtained.¹⁹ These results, summarized in Fig. 4, show that significant barriers persist even when faceted crystal shapes are far from equilibrium.

We have also considered the barriers for shape changes of crystals that contain continuously curved (rough) surfaces in addition to the flat facets.¹⁷ As a model, we consider crystals whose equilibrium shapes are a sphere truncated on either end by a flat facet. We take the energy of the singular surface to be σ_s and the energy of the curved surface to be σ_c . The relative value of these energies is taken to be $\sigma_s/\sigma_c = \cos\theta$, where the angle, θ , is defined with the other geometric parameters in Fig. 5a. Following Herring²⁰, the free energy $\epsilon_\theta(r)$ needed to create a circular partial layer of height a and radius r on the circular facet of radius ρ , using material taken from a bulk reservoir with a chemical potential of $\mu = 0$, is:

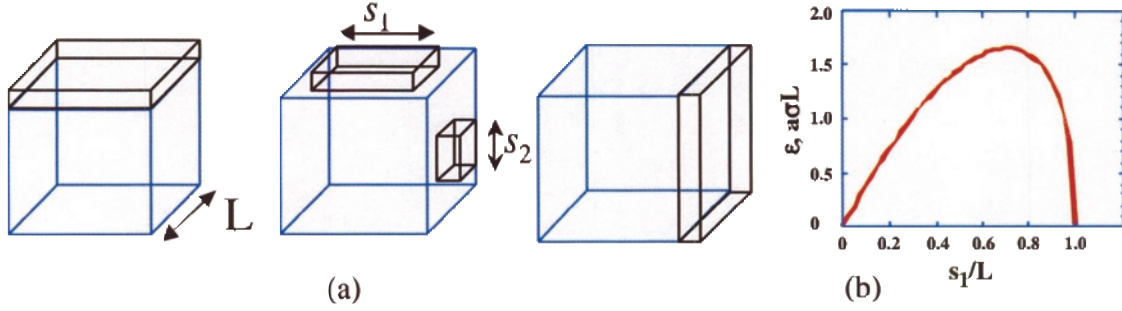


Figure 3. (a) a layer of atoms is transferred from the top of the crystal to the side. (b) Eq. 1.

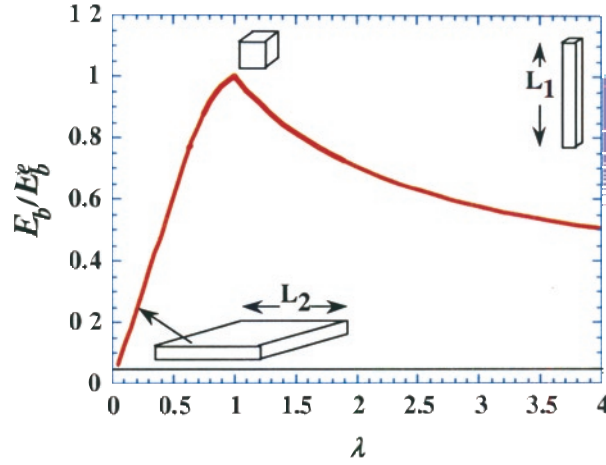


Figure 4. The NEB (E_b) for fully faceted crystals whose equilibrium shape is a cube, as a ratio of the barrier for fluctuations about the equilibrium shape (E_b^e). The horizontal axis gives the axial ratio, where $\lambda = (L_1/L) = (L_1/(\text{Volume})^{1/3})$.¹⁹

$$\varepsilon_0(r) = 2\pi ar \left[\frac{-\sigma_s}{\tan \theta} + \frac{\sigma_c}{\sin \theta} \right] = 2\pi ar \sigma_c \sin \theta \quad (2)$$

We assume that Eq. 2 holds when the height of the step is as small as a single atomic layer.

To analyze fluctuations about the equilibrium shape, we consider the transfer of a fixed volume (πar^2) of material from the curved surface of chemical potential $2\sigma_c/R$ to the ideal singular surface to form the partial layer described above. The total required free energy is:

$$\varepsilon_i(r) = 2\pi ar \sigma_c \sin \theta - \pi ar^2 \left(\frac{2\sigma_c}{R} \right) = 2\pi a \sigma_c \sin \theta \left(r - \frac{r^2}{\rho} \right) \text{ for } 0 \leq r \leq \rho, \quad (3)$$

where $\rho = R \sin \theta$ is used in the last step. This expression also gives the energy required for a reverse transfer of all but a nucleus of radius r from the facet to the curved surface (i.e. $-\varepsilon_i(r - \rho) = \varepsilon_i(r)$). Note that the nucleus has a positive free energy for all values of $0 \leq r \leq \rho$ and that, as required by equilibrium, there is no net change in free energy to transfer a complete facet layer in either direction (see Fig. 5b). The maximum of Eq. 3 occurs at $r = r^* = \rho/2$ corresponding to a barrier height of:

$$E_b = \pi ar^* \sigma_p = \frac{1}{2} \pi a \rho \sigma_c \sin \theta = \frac{1}{2} \pi a R \sigma_c \sin^2 \theta \quad (4)$$

Note that the barrier is symmetric with respect to addition or removal of a complete facet layer, and this is consistent with the requirement that the two processes have equal probability in equilibrium. As with the

case of the cube, the barrier energy is linear in the particle or facet size (for a given θ). Using the same physical parameters as for the cube, we estimate from Eq. 4 that the limiting particle diameters for crystal with $\theta = 20^\circ$, 10° , and 5° , are 7.3, 28.1, and 112 nm, respectively. We therefore see that the limiting sizes are larger than for the cube and decrease as the surface energy anisotropy increases. In all cases, there is still a size above which rates will be limited by nucleation.

Following a similar line of reasoning, the NEB for distorted (nonequilibrium) variants of the truncated sphere to evolve to equilibrium have also been evaluated and the results are summarized in Fig. 6.¹⁹ This analysis reveals two noteworthy trends. First, prolate (elongated) crystals are able to evolve to shapes that are closer to equilibrium than the oblate (foreshortened) shapes. Second, as the surface energies become more isotropic, prolate shapes can more nearly approach the equilibrium shape.

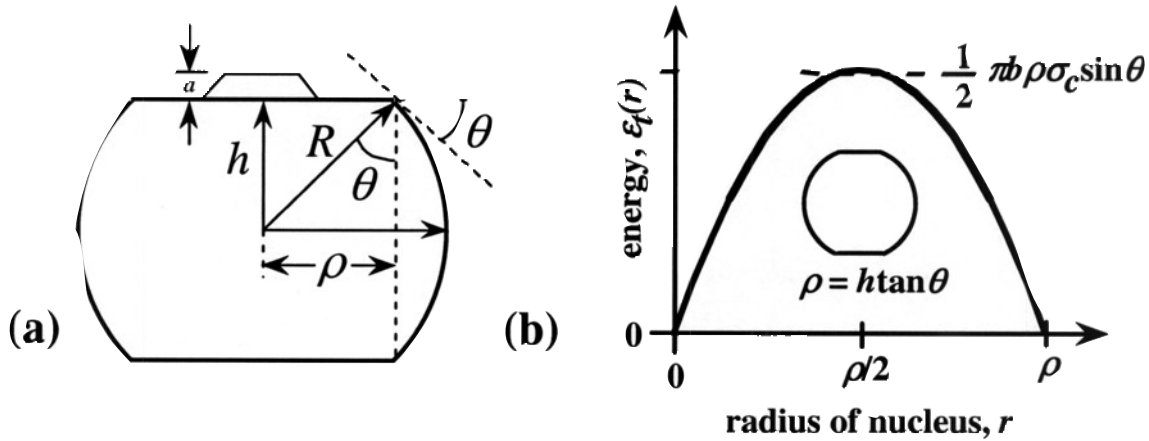


Figure 5. Geometry for the truncated cube model and (b) a graph of Eq. 3.

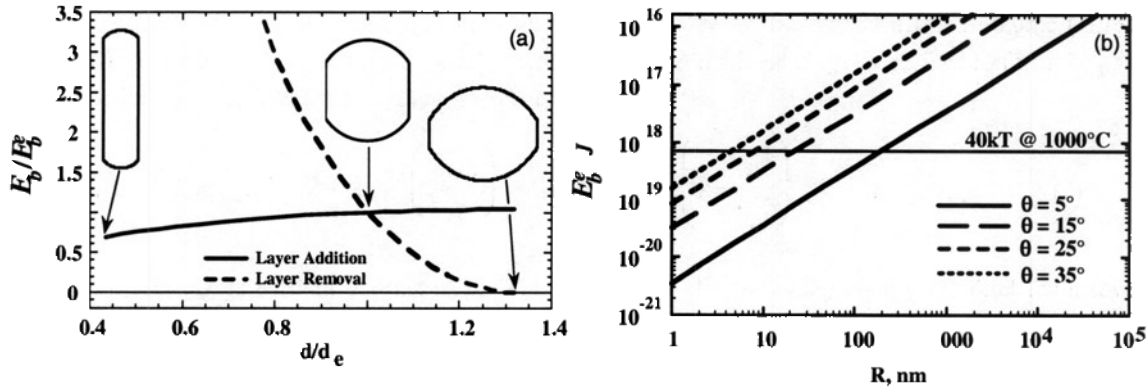


Figure 6. (a) The layer addition (solid line) and removal (dashed line) barriers for crystals with $\theta = 35^\circ$. Inset in the figure are axial sections of the oblate shape, for which $d/d_e = 0.43$ (left), the equilibrium shape, for which $d/d_e = 1$ (middle), and the prolate shape, for which $d/d_e = 1.32$. (b) Values of the NEB for equilibrium crystals with $\theta = 5^\circ$, 15° , 25° , and 35° as a function of R . These values were calculated assuming $\sigma_c = 1 \text{ J/m}^2$ and $a = 3 \times 10^{-10} \text{ m}$. The horizontal line is added to indicate the energy of 40 kT at 1000°C .¹⁹

Coarsening

To determine how the NEB influences the coarsening of faceted crystals, we consider a cube that is able to exchange matter with a reservoir at a fixed chemical potential (μ_∞). As before, the crystal has its

equilibrium shape and an edge length of $L=2R$; consider the case where $\mu_\infty > 2\sigma/R$ so that there is a small driving force for the cube to grow. The reservoir itself can be thought of as a large number of identical cubes of the same material with edge length $2R^*$ so that $\mu_\infty=2\sigma/R^*$. Now consider the transfer of material from the reservoir to the crystal. To do so, a square nucleus of area s^2 and height a must be placed on the facet. The energy for this transfer is:

$$\varepsilon(s) = 4as\sigma - as^2 \frac{2\sigma}{R^*}, \quad (5)$$

for $0 \leq s \leq L$. In Eq. 5, the first term on the right hand side is the energy of the perimeter of the nucleus and the second term is the change in the free energy on moving a volume of material (as^2) from the reservoir to the flat surface. Note that if the crystal is in equilibrium with a reservoir of identical particles ($R^*=L/2$), then there should be no energy change when a single layer of atoms is transferred from the reservoir. Equation 5 shows that this is the case when $s=L$ and $R^*=L/2$. However, to add even a single layer, the crystal must pass through a relatively higher energy state that contains a partial layer. By differentiation of Eq. 5, we see that the maximum occurs at $s = R^*$ and that the barrier to addition, ε_+ , is:

$$\varepsilon_+ = 2a\sigma R^* \quad (6)$$

where R^* is between 0 and L . In this case, the NEB is independent of the crystal size for all crystals with $R \geq R^*$. If we assume the same physical quantities as before, then the crystals will grow only when R^* is less than a critical value of about 1.5 nm. In other words, only crystals with $L \sim 3$ nm can provide supersaturation that is high enough to drive nucleation on a flat facet. If we take R^* as a representation of a mean crystal size in a distribution, then as soon as R^* rises above the critical value, the NEB will halt growth.

If we next consider the situation where $\mu_\infty < 2\sigma/R$, so that there is a driving force for the cube to shrink, an expression analogous to Eq. 5 can be written and we can show that the barrier for layer removal is:

$$\varepsilon_- = 2a\sigma \left[R^* + L \left(\frac{L}{R^*} - 2 \right) \right] \quad (7)$$

where R^* is between $L/2$ and L . Note that for a crystal in contact with a reservoir of identical particles ($R^* = L/2$), $\varepsilon_+ = \varepsilon_- = 2a\sigma R^*$, as we would expect for the equilibrium case. The barrier to remove a layer is smaller if the reservoir is made up of crystals that are somewhat larger ($L/2 < R^* < L$) and vanishes completely if the particles in the reservoir are twice as large as the crystal ($R^* \geq L$). These conclusions are represented in Fig. 7.

To simulate how a system of crystals with a dispersion of grain sizes coarsens, a numerical model has been developed that allows a distribution of crystals to evolve with time.²¹ The continuum model uses the mean field approach and has been described in detail previously.²¹ Briefly, a discrete particle size distribution, $n(R)$, is defined at the start of the simulation. Crystals in each discrete size class are in equilibrium with a chemical potential of $\mu_e = 2\sigma/R$ and are embedded in a medium with a mean field chemical potential $\mu_\infty = 2\sigma/R^*$, where R^* is the size of a crystal that neither grows nor shrinks. To incorporate the NEB, it is assumed that the rates of diffusion to or away from crystals of a given size class are equated to the rates at which nucleation can occur on the same crystals. To accomplish this, a uniform surface chemical potential, μ_s , is defined for each size that balances the rate. So, for a given distribution, $n(R)$, the value of

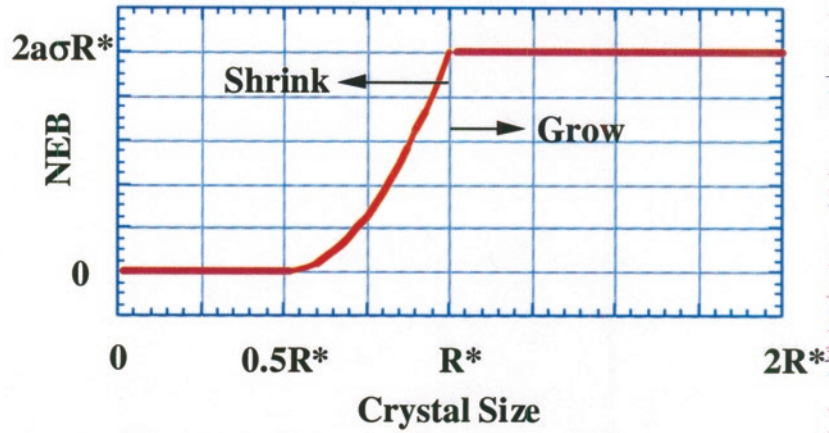


Figure 7. The NEB for crystals of different sizes in contact with a reservoir of crystals with size R^* .

R^* is numerically determined. Next, using the constraint that the total volume must be conserved after an increment of time, the surface chemical potentials $\mu_s(R)$ are determined for each size class. This allows the sizes in the next instant of time to be determined and repetition of this algorithm allows the dynamics of the distribution to be studied.

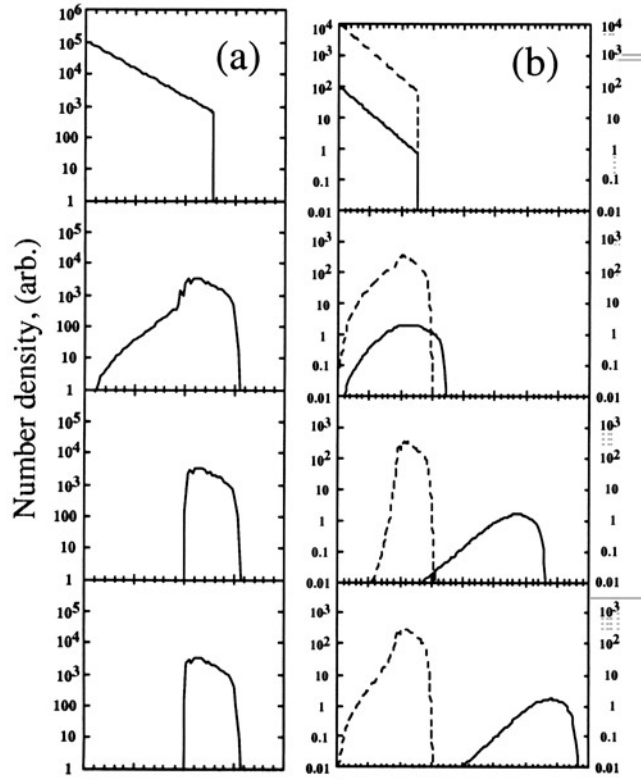


Figure 8 (a) Time evolution of a particle distribution at, from top to bottom, 0, 0.03, 0.1, and 0.57 sec, $\sigma = 0.1 \text{ J/m}^2$. In this case, the growth is NEB limited. (b) Simultaneous evolution of the defect-free (dashed line) and defective (solid line) particle populations. From top to bottom, 0, 0.01, 0.08, 0.11 sec.²¹

When the simulations are run under the assumption that the surface energy is unrealistically small (0.001J/m^2), then the NEB is insignificant and crystals coarsen according to kinetics predicted by Lifshitz, Slyozov¹, and Wagner² (LSW) for crystals with rough surfaces. On the other hand, if realistic surface energies are used, and all crystals are assumed to be ideal with no step-producing defects, then the crystals coarsen to a point where thermal fluctuations can no longer drive nucleation (see Fig. 8a). Finally, when there is a mixture of ideal crystals with no pre-existing defects, and crystals with persistent step sources that can grow or shrink without a barrier, the defective crystals grow at the expense of the perfect crystals and a bimodal grain size distribution develops (see Fig. 8b).

The Kinetically Locked Size Regime

All of the calculations described above imply that the kinetics of morphology changes and coarsening of faceted crystals are influenced by both the crystal size and defect structure. We therefore hypothesize that there is a kinetically locked size regime where the size and the morphology of defect-free crystals will be static. This idea is represented schematically in Fig. 9. The curve with a positive slope from the origin divides the upper regions of the map, where thermal fluctuations can drive nucleation from the lower regions, where the NEB limits shape changes. As the crystal size increases, the NEB increases and higher temperatures are required to generate the fluctuations necessary for nucleation. When the crystal becomes large enough, the presence of a step-producing defect is virtually guaranteed and the NEB is no longer effective in immobilizing the crystal. In Fig. 9, this boundary was arbitrarily placed at 10^4 nm , but it should be recognized that the necessary defects will be statistically distributed and this distribution will vary with both the type of material and the manner in which it was prepared.

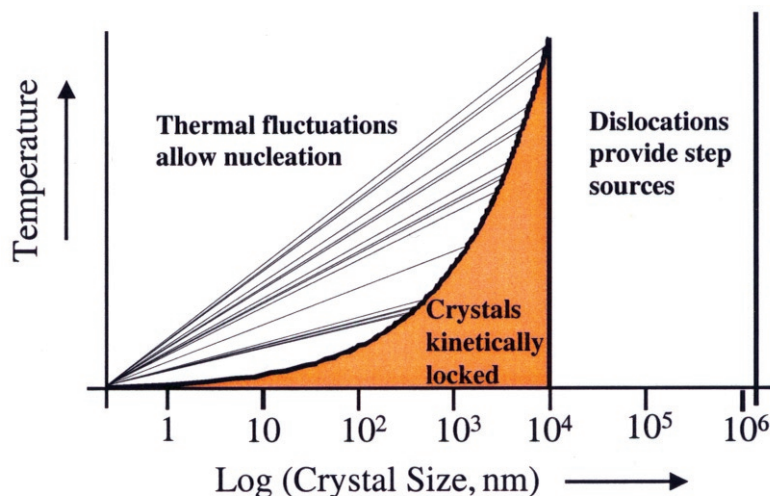


Figure 9. Schematic illustration of the kinetically locked size regime, where nucleation is required for morphological changes.

Experimental Support for the Kinetically Locked Size Regime

There are many experimental observations that provide evidence to support the existence of a NEB for shape changes²²⁻³². This evidence has been summarized previously¹⁹; for brevity, only two of the most compelling observations are described here. First, the kinetics of the shape transformation of Pb spheres and plates supported on graphite have been compared.²⁶ The Pb crystals used in this study had radii between 0.5 and $5\text{ }\mu\text{m}$. Small molten spheres of Pb supported on graphite, when crystallized, reached an apparent (nearly spherical) equilibrium form in about 4 hours at $250\text{ }^{\circ}\text{C}$. However, when tabular crystals

were annealed at the same temperature for up to 160 h, only a subset of the crystals reached the same apparent equilibrium state; the remainder maintained oblate shapes. We surmise that this is because of the asymmetry of the NEB for the two cases, as illustrated in Fig. 6a. For a tabular crystal to convert to a more spherical one, the large facet must shrink and advance away from the center of the crystal and the NEB for this process remains significant even at large deviations from equilibrium. However, as facets grow on the spherical crystal, the NEB becomes significant only when the particle closely approximates its equilibrium shape. The second observations of interest, on the kinetics of the morphological evolution of oblate cavities ($20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m} \times 0.5\text{ }\mu\text{m}$) in sapphire, were reported by Kitayama et al.³¹ The cavities were annealed at $1900\text{ }^{\circ}\text{C}$ for up to 16 h. While some of the cavities evolved to a reproducible equilibrium shape, others maintained a stationary oblate morphology. The authors suggested that the immobilized shapes were defect free, while those that evolved to equilibrium contained step-producing defects.

The role of defect-assisted growth in the abnormal coarsening of faceted crystals has been discussed qualitatively in a number of papers during the last six years.³³⁻³⁹ For example, qualitative observations suggest that twin plane reentrant edges in barium titanate³⁷ and dislocations in strontium titanate³⁸ can lead to accelerated growth. A more recent study of coarsening in the lead magnesium niobate - lead titanate system demonstrates that faceted crystals with step-producing defects grow abnormally large at the expense of more perfect matrix crystals³⁹, as predicted by the coarsening simulations described above (see Fig. 8b).²¹

Summary

Consideration of the mechanisms by which faceted crystals change shape has led us to hypothesize the existence of a 'kinetically locked' size regime where faceted crystals maintain stationary, nonequilibrium shapes. Depending on the physical characteristics of the system, the size range will be between 10 and 10,000 nm. The lower limit of the size range will increase with temperature and the upper limit of the range will be determined by the occurrence of persistent step sources such as screw dislocations and reentrant twin plane edges. This hypothesis can be applied to understand the bimodal crystal size distributions that develop during abnormal coarsening.

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SELF-PROPAGATING FRONTAL POLYMERIZATION IN WATER AT AMBIENT PRESSURE

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Introduction

Advances in polymer chemistry have led to the development of monomers and initiation agents that enable propagating free-radical polymerization fronts to exist. These fronts are driven by the exothermicity of the polymerization reaction and the transport of heat from the polymerized product to the reactant monomer/solvent/initiator solution. The thermal energy transported to the reactant solution causes the initiator to decompose, yielding free radicals, which start the free radical polymerization process as discussed in recent reviews^{1,2}. The use of polymerization processes based on propagating fronts has numerous applications. Perhaps the most important of these is that it enables rapid curing of polymers without external heating since the polymerization process itself provides the high temperatures necessary to initiate and sustain polymerization. This process also enables more uniform curing of arbitrarily thick samples³ since it does not rely on heat transfer from an external source, which will necessarily cause the temperature history of the sample to vary with distance from the surface according to a diffusion-like process. Frontal polymerization also enables filling and sealing of structures having cavities of arbitrary shape without having to externally heat the structure.

Water at atmospheric pressure is most convenient solvent to employ and the most important for practical applications (because of the cost and environmental issues associated with DMSO and other solvents). Nevertheless, to our knowledge, steady, self-propagating polymerization fronts have not been reported in water at atmospheric pressure. Currently, polymerization fronts require a high boiling point solvent (either water at high pressures or an alternative solvent such as dimethyl sulfoxide (DMSO) (boiling point 189°C at atmospheric pressure.) Early work on frontal polymerization⁴, employed pressures up to 5000 atm in order to avoid boiling of the monomer/solvent/initiator solution. High boiling point solutions are needed because in order to produce a propagating front, a high front temperature is needed to produce sufficiently rapid decomposition of the free radical initiator and subsequent free radical polymerization and heat release at a rate faster than heat losses remove thermal energy from the system. (While the conduction heat loss rate increases linearly with temperature, the free radical initiator decomposition is a high activation energy process whose rate increases much more rapidly than linearly with temperature, thus as the temperature decreases, the ratio of heat loss to heat generation increases, eventually leading to extinction of the front if the temperature is too low.)

In order to obtain atmospheric pressure frontal polymerization in water, it is necessary to identify a monomer/initiator combination that is water soluble and will not extinguish even when the peak temperature (T^*) is less than 100°C. In this work acrylic acid (AA) was chosen as the monomer because

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is it one of the most reactive monomers and can polymerize readily at low temperatures even without initiators. Ammonium persulfate (AP) was chosen as the initiator because it decomposes readily at low temperatures, produces relatively few bubbles and is commercially available. The propagation rates and extinction conditions of the fronts are studied for a range of AA and AP concentrations. Small amounts of fumed silica powder (Cab-o-sil, Cabot Corporation) were added to the solutions to inhibit buoyancy-induced convection in the solutions; future studies will investigate the effects of buoyant convection within the solutions.

Experiments

Experiments were conducted at ambient temperature ($22 \pm 2^\circ\text{C}$) using standard glass tubes of approximately 16 mm inside diameter, 1.1 mm wall thickness and 100 mm length. Acrylic acid (minimum purity 99%, inhibited with 200 ppm monomethyl ether hydroquinone to prevent spontaneous polymerization) and ammonium persulfate (98% minimum purity) were used as received from the suppliers. Solutions were prepared by making an AP-water mixture, mixing in Cab-o-sil, then finally adding the AA. This procedure minimized the time that AP and AA were mixed before the experiment was conducted, which in turn minimized the opportunity for pre-reaction. To verify that no significant pre-reaction was occurring, a few tests were conducted in which the mixed solutions were allowed to stand for periods of up to one hour before conducting the experiments. No significant change in the properties of the fronts was observed over this period. In contrast, a few tests performed using DMSO solvent rather than water did show substantial pre-reaction effects within a few minutes. Consequently, tests using DMSO solvent were not pursued further.

Mixed solutions were poured into the glass tube and ignited at the top using an electrically heated wire. The resulting downward propagating fronts were imaged using a standard video camera. From plots of front position vs. time, the instantaneous front speed could be determined. After an initial transient, either a steadily propagating front (constant propagation speed (S)) developed or the front extinguished. For some tests the front temperatures were measured using a type K thermocouple that was immersed in the solution with its junction about 30 mm from the bottom of the tube.

It was found that only a certain range of AA and AP concentrations produced steadily propagating fronts that neither extinguish due to too low peak temperatures nor bubble violently due to peak temperatures above the solution boiling point. Figure #1 shows these ranges. The limiting condition for bubbling depends mostly on the AA concentration and only weakly on the AP concentration. This is reasonable because the theoretical adiabatic front temperature (T_a) depends primarily on the heat release due to conversion of monomer to polymer, which in turn depends on AA concentration. AP concentration does have a slight effect on this limit, however, because, as discussed later, AP affects the front speed that in turn affects the ratio of heat loss to heat generation and thus affects the peak temperature, even for compositions with the same theoretical adiabatic T_a . The limiting condition for steadily propagating fronts that do not extinguish depends significantly on both AA and AP concentrations because, as discussed later, S is nearly constant at the limit and (as Figure #2 shows) S depends on both T_a (which depends mostly on AA concentration) as well as the initiator (AP) concentration.

Tests were also conducted in which the glass tube was immersed in a stirred water bath in order to obtain a nearly isothermal ambient wall temperature. For reasons suggested below, no conditions could be found for which the fronts were neither extinguished nor bubbling.

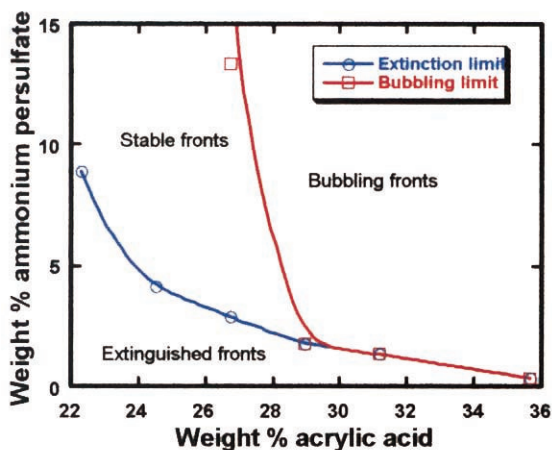


Figure 1. Effect of mass percent of AA on limits to steady and bubbling frontal polymerization in AA/AP/water solutions with 3.6 mass percent Cab-o-sil added to suppress buoyant convection.

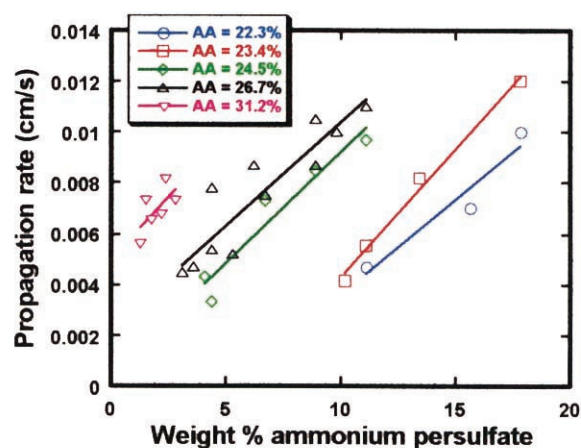


Figure 2. Effect of mass percent AP and AA on rates of steady frontal polymerization in AA/AP/water solutions with 3.6 mass percent Cab-o-sil.

Figure #2 shows propagation speeds for the full range of AA and AP concentrations for which steady values of S could be measured. This includes some conditions at higher AA concentrations for which bubbling was observed but was not so substantial that steady values of S could not be determined. It is interesting to note that

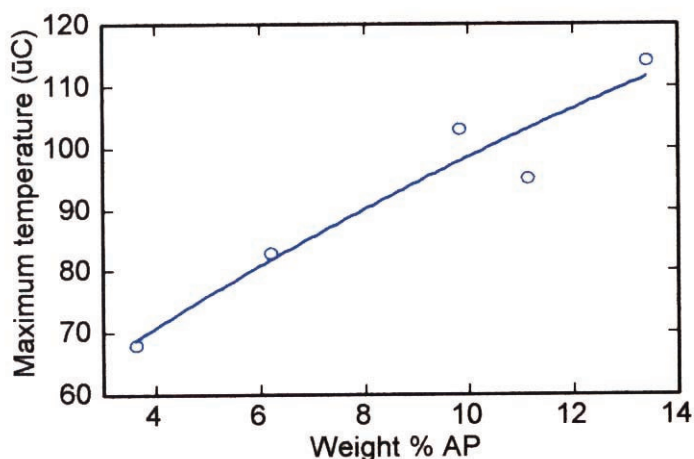


Figure 3. Effect of mass percent AP on the maximum temperature of steady frontal polymerization in AA/AP/water solutions with 26.7 mass percent AA and 3.6 mass percent Cab-o-sil.

the minimum steady value of S (*i.e.*, at the extinction limit) is nearly the same for each mass fraction of AA. The mean value of S at the extinction limit is 0.0048 cm/s with a standard deviation that is 13% of the mean. The corresponding Peclet number at the limit ($= Sd/\alpha_s$, where α_s is the thermal diffusivity of the solution (approximated as water for the purpose of estimating thermal properties) and d the tube diameter), which has a mean value of $(0.0048 \text{ cm/s})(1.6 \text{ cm})/(0.0015 \text{ cm}^2/\text{s}) = 5.1$, where α_s (and all subsequently required thermal properties) will be based on the average of the ambient temperature and the peak temperature T^* .

Figure #3 shows the measured values of T^* during front passage for one value of AA mass fraction (0.267) and several values of the AP mass fraction. Note that except for the point on this plot corresponding to the highest AP concentration, values of T^* are close to or below 100°C . Consistent with this information, Figure #1 shows that only the highest point exhibited bubbling.

Discussion

Following standard combustion theory (Williams, 1985), a theoretical value of the Peclet number at the extinction limit is estimated by determining the value of Pe for which the ratio of heat loss rate across the front thickness to heat generation rate is of the order $1/\beta$, where $\beta \equiv E/RT^*$ is the non-dimensional activation energy, E is the apparent overall activation energy for the chemical reaction and R is the gas constant. The slope of a plot of $\ln(S)$ vs. $1/T^*$, where T^* must be on an absolute scale, is $-E/2R$. From this plot (not shown), a value of $E \approx 13.5$ kcal/mole is inferred. For the limit mixture at 0.267 mass fraction AA, whose peak temperature is 68°C , $\beta = 19.9$ can then be estimated.

Unlike gas combustion theory, it is inappropriate to presume ambient wall temperature in order to estimate the rate of heat loss. Instead, for the polymerization fronts (whose solutions have much higher thermal conductivity than fuel-air mixtures), it can easily be shown that the main source of thermal resistance is between the wall of the tube and ambient air, rather than between the hot products and the tube wall itself. In this case the heat loss rate is given by $Nu(k_g/d)A\Delta T$, where Nu is the Nusselt number for buoyant convection heat transfer from the tube wall to ambient, k_g the gas thermal conductivity, d the tube diameter, A the area exposed to heat transfer (in this case the flame thickness multiplied by the perimeter of the tube $= \pi d$), and ΔT the temperature difference between the tube wall and ambient. The rate of heat generation is $\rho C_p S A' \Delta T$, where ρ is the solution density, C_p its specific heat, and A' the cross-sectional area of the tube $= \pi d^2/4$. The ratio of the heat loss to heat generation is then $4Nu(k_g/k_s)Pe^2$, where k_s is the thermal conductivity of the solution. If this ratio is $1/\beta$ at extinction, then Pe at extinction is given by $[4\beta Nu(k_g/k_s)]^{1/2}$. To estimate the Nusselt number we assume buoyant convection on a vertical wall in air whose height is the flame thickness δ ($\delta \approx \alpha/S = (0.0015 \text{ cm}^2/\text{s})/(0.0048 \text{ cm/s}) = 0.31 \text{ cm}$) and width is πd . The corresponding Rayleigh number (Ra) is $g(\Delta\rho/\rho)d^3/\nu\alpha$ where $\Delta\rho/\rho$ is the fractional density change (estimated as 0.22 based on the measured limit temperature and the ideal gas law) and ν the kinematic viscosity of air. Thus (again using temperature-averaged properties) $Ra \approx (981 \text{ cm/s}^2)(0.22)(0.31 \text{ cm})^3/((.17 \text{ cm}^2/\text{s})(.25 \text{ cm}^2/\text{s})) = 150$. For a vertical plate in air with $Ra = 150$, $Nu \approx 3.3$. Using $Nu = 3.3$, $\beta = 19.9$, $k_s = 0.63 \text{ W/mK}$ (taken as that of water), $k_a = 0.028 \text{ W/mK}$, we obtain $Pe = 3.4$ at the extinction limit. Despite the simplicity of the model employed, this value is reasonably close to that seen experimentally and suggests that heat loss to ambient via buoyant convection is the mechanism of extinction for the data shown in Figure #1.

For the isothermal tube walls (corresponding to our experiments in which the tubes were placed in a stirred water bath), the same type of analysis as that presented in the previous paragraph can be used to predict that the limit Peclet number would be $[4\beta Nu]^{1/2} \approx 17$, where in this case $Nu = 3.75$ is the value for convective heat transfer for laminar pipe flow with isothermal walls. In a 16 mm diameter tube, this value of limit Pe would require $S \geq 0.016 \text{ cm/s}$. With $E = 13.5$ kcal/mole and $S = 0.0048 \text{ cm/s}$ at $T^* = 68^\circ\text{C}$, we can infer that $T^* \geq 115^\circ\text{C}$ would be required to obtain $S \geq 0.016 \text{ cm/s}$. Thus, for a 16 mm diameter tube with isothermal, ambient temperature walls, bubbling would always be expected at atmospheric pressure for any solution having a high enough value of S to avoid extinction. Another means to avoid extinction is by using larger diameter tubes that would allow lower S for the same Pe . According to our estimate of activation energy,

a value of T^* of 100°C corresponds to $S \approx 0.010$ cm/s. For a limit Pe of 17, the corresponding d is about 25 mm. Thus, for sufficiently large tubes, it should be possible to obtain solutions that do not extinguish nor bubble even for isothermal, ambient temperature wall boundary conditions.

Summary and conclusions

Frontal polymerization at ambient pressure using water as the solvent has been demonstrated by using a very reactive monomer (AA) and free-radical initiator (AP) that enabled self-propagating free-radical polymerization fronts to occur at temperatures below 100°C. The range of AA and AP concentrations producing polymerization fronts is limited by extinguishments via heat losses at low AA and AP concentrations, and boiling at high concentrations. The heat losses leading to extinction appear to be due to buoyant convection from the tube wall to ambient air. When the wall condition is isothermal, the range of compositions exhibiting propagating fronts is much smaller and no AA and AP concentrations exhibited non-bubbling fronts. It is shown, however, that with sufficiently large tubes, non-bubbling propagating fronts could probably be obtained. It is suggested that frontal polymerization in water at ambient pressure could lead to new practical applications because of the cost and environmental issues associated with solvents other than water and the inconvenience of using pressures higher than atmospheric to avoid boiling.

Acknowledgements

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SURFACE AND INTERFACIAL STRUCTURES INDUCED BY ELECTROHYDRODYNAMIC INSTABILITIES

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It is well known that there is thermally excited capillary wave at the interface, where the amplitude and wavelength are governed by the interfacial tension and any pressures acting on the interface including gravity. An external electric field applied across the interface exerts an electrostatic pressure on the interface that will amplify the fluctuations. The electrostatic pressure works against interfacial tension, which is given by the product of the interfacial energy and the interface area, to generate the electrohydrodynamic instabilities. The small wavelength fluctuations are suppressed since they are too costly energetically. The long wavelength fluctuations, on the other hand, are also suppressed due to the fluid dynamics. This leads to the fastest growth of one wavelength, which is amplified, and eventually bridges between two electrodes. Figure 1 shows the general sample configuration in our studies. The indium-tin-oxide coated (ITO) microscope slides is served as the upper electrode. It is transparent and good for real time optical microscopy observations. The separation distance between Si substrate and ITO glass can be controlled by evaporating thin rails of SiOx on the top of ITO glass or Si substrate as an insulating spacer. In the case of single layer film and bilayer studies, the medium 1 and the medium 2 are air/liquid, and liquid 1/liquid 2, respectively.

A simple linear stability analysis indicated that the instability exhibits a well-defined lateral wavelength that follows a power-law dependence on the applied electric field, in agreement with theory.^{1,2} We extend this theoretical model in terms of characteristic wavelength at liquid/air interface to more general case for liquid/liquid bilayer and obtain experimental data to support and contest the model. The characteristic wavelength at the interface of liquid/liquid bilayer can be given as^{3,4}

$$\lambda = \frac{2\pi}{U \left| \frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right|} \left(\frac{\gamma_{12}}{\epsilon_0} \right)^{1/2} \left(\frac{d-h_0}{\epsilon_1} + \frac{h_0}{\epsilon_2} \right)^{3/2} \quad (1)$$

where $d-h$ and h are the film thicknesses of liquid 1 and liquid 2 with dielectric constants ϵ_1 and ϵ_2 , respectively. γ_{12} is the interfacial tension between liquid 1 and 2, and ϵ_0 is the dielectric permittivity in vacuum.

The central finding in liquid/liquid bilayer study is a reduction of the length scale of dynamical instabilities induced by an electric field when the air/liquid interface is replaced by a liquid/liquid interface. A typical example is shown in Figure 2. In the first set of experiments, a layer of 140nm PI, leaving an air gap of

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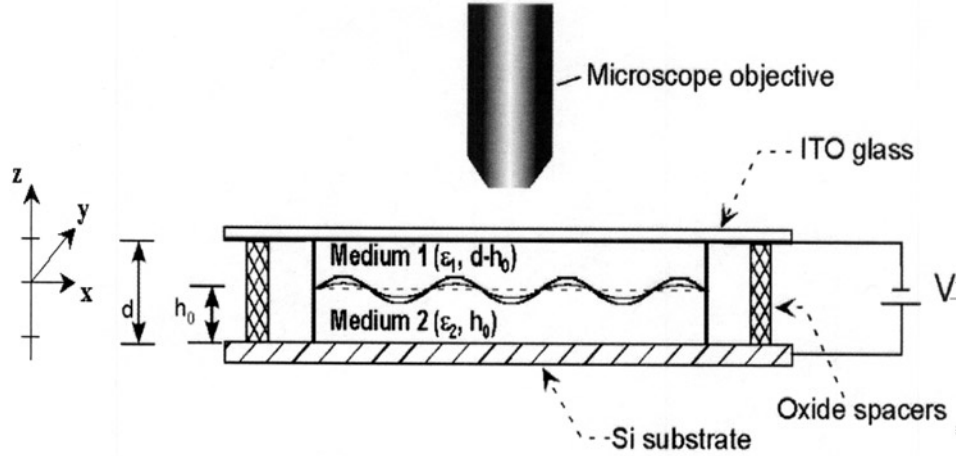


Figure 1. Sketch of the sample geometry used in the experiments. A bilayer of two liquids with film thickness of h_0 and $d-h_0$, respectively, is confined between two solid electrodes: a highly polished silicon wafer (lower electrode) and an ITO coated microscope slide (upper electrode). The distance between the two electrodes is controlled by the height of spacer structures (SiO_x) evaporated at the edges of the slides on top of the ITO. The temporal evolution of the confined samples under an applied electric field is studied by optical microscopy in the reflectance mode.

940 nm, is exposed to 20V electric field. An amplification of fluctuations at the PI/air interface is occurred, ultimately leading to the creation of an array of vertically standing PI columns (Figure 2a). The average distance between the center of two neighboring columns is $\langle d_{\text{cyl-cyl}} \rangle = 47.4 \pm 4.4 \mu\text{m}$. The influence of changes in ϵ and γ of the upper layer on the time and size scales of the evolving structures was investigated in the second set of experiments. Figure 2b shows the final state of a PI/ODMS bilayer annealed at ambient conditions. A visual comparison of Figures 2a and b shows a clear reduction in length scale, associated with the replacement of air by ODMS. The cylinder structures now exhibit a typical spacing of $\langle d_{\text{cyl-cyl}} \rangle = 20.6 \pm 1.3 \mu\text{m}$. This spacing is about one-half that observed in the single film experiments.³

A systematic characterization of structure formation at the interface of liquid/liquid bilayers in the electric field is also reported here. Regardless of the polymers used, very good agreement over many orders of magnitude in reduced wavelength and field strength is observed using no adjustable parameters. An optical micrograph of the PS/PDMS bilayer after one day under a 50V is shown in Figure 3a. Columns of PS through the upper PDMS layer are evident in the micrograph. The formation of the cylindrical structures at the interface is clearly seen. A 2D Fast Fourier Transform (FFT) of the optical micrograph is shown in the inset. The appearance of a ring in the transform indicates that there is a well-defined center-to-center distance between adjacent PS columns of PS of $13.0 \mu\text{m}$. After removing the upper PDMS layer with heptane, AFM was used to examine the surface of the underlying PS layer, i.e. the interface between the PDMS and PS layers. Shown in Figure 3b is the AFM image of the PS surface obtained in the height mode. As seen, columns of PS have been produced by the electrostatic pressure acting on the original PDMS/PS interface. The average size of the columns is $8.5 \pm 0.3 \mu\text{m}$ with an average center-to-center distance between adjacent PS columns of $13.0 \pm 1.0 \mu\text{m}$. Shown in the inset is a 2D FFT of the AFM image. The six spots evident in these data indicate that, locally, there is a hexagonal symmetry in the lateral arrangement of the columns. Substituting the relevant parameters for the PDMS/PS bilayer case into equation (1) yields a characteristic distance of $15.8 \mu\text{m}$, which agrees well with the $12.9 \mu\text{m}$ value measured experimentally.⁴

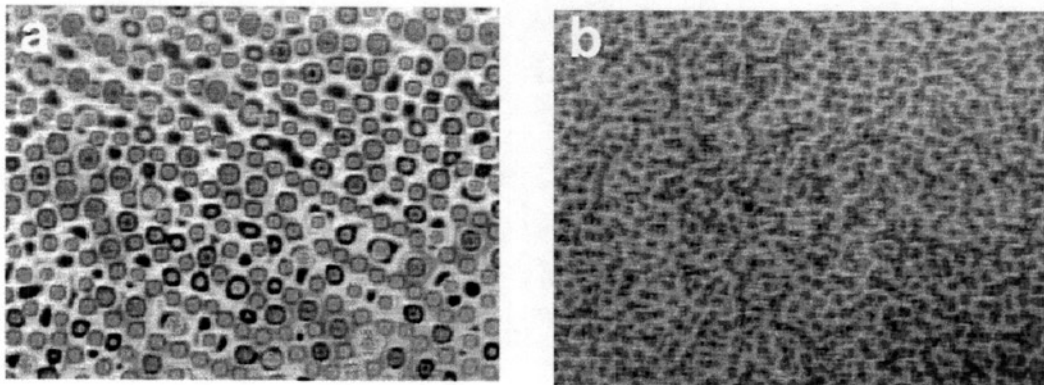


Figure 2. a) Optical microscopy image of a thin liquid film of polyisoprene, b) Optical microscopy image of a bilayer of polyisoprene and oligomeric dimethylsiloxane annealed for 2 days in an electric field ($d-h = 940$ nm, $h = 140$ nm, $V = 20$ V). In both figures the original color images were converted to gray scale. The dimensions of the images are $528 \mu\text{m}$ by $692 \mu\text{m}$.

In a second set of experiments, the upper PDMS layer was replaced by a PMMA layer to form PS/PMMA bilayer. Since the interfacial tension between PS and PMMA ($\gamma_{\text{PS/PMMA}} = 1.1 \text{ mN/m}$ at 170°C) is smaller than that for a PS/PDMS bilayer, ($\gamma_{\text{PS/PDMS}} = 6.1 \text{ mN/m}$) at any given temperature, then, from equation (1), it would be expected that the characteristic wavelength λ would decrease. Shown in Figure 4a is the optical micrograph of the PS/PMMA bilayer after one day at 170°C with 30V applied after selectively removing the upper PMMA layer. Direct images of the bilayer without removal of the upper layer were not easily seen, since the refractive indices of PS and PMMA, 1.591 and 1.49 , respectively, are very similar. The 2D FFT shown in the inset exhibits a ring, indicative of a well-defined separation distance between the features at the interfaces. Analysis of the optical micrograph yields an average center-to-center distance

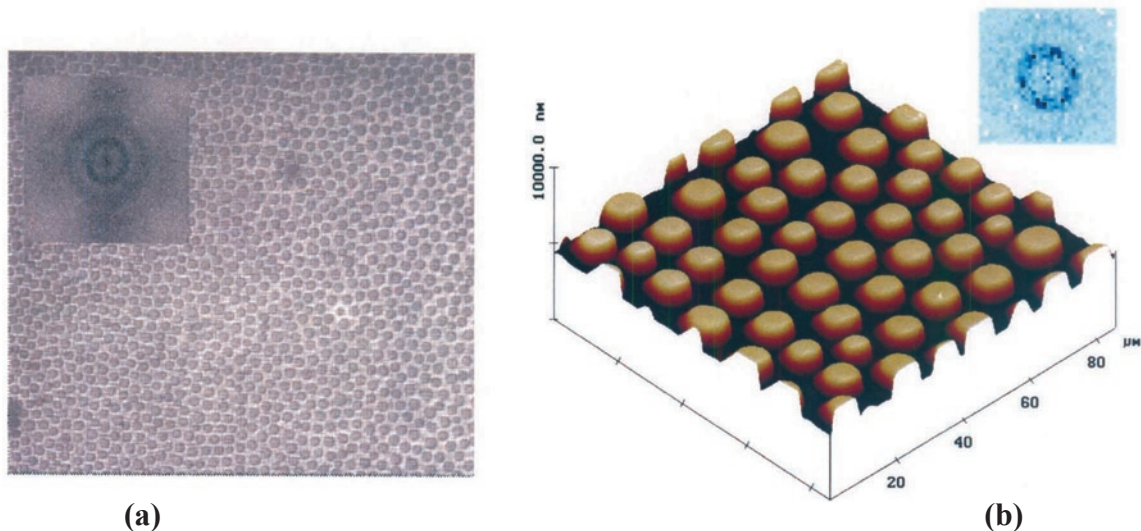


Figure 3. (a) Optical micrograph of a PS ($h_{\text{PS}} = 550 \text{ nm}$) / PDMS ($h_{\text{PDMS}} = 700 \text{ nm}$) bilayer exposed to 50V at 170°C for one day. The image size is $438 \times 398 \mu\text{m}^2$. The original color images were auto leveled and contrasted, and then converted to a grayscale to enhance the weak contrast due to the small refractive index difference between PS and PDMS. The inset shows the 2D fast Fourier transform (FFT) pattern of the corresponding optical micrographs. (b) The 3D AFM height image of the PS/PDMS bilayer after removal of the upper PDMS layer with heptane. The 2D FFT of the AFM image is shown in the inset.

between adjacent features of $4.0 \pm 0.7 \mu\text{m}$ with an average diameter of the columns of $1.7 \pm 0.3 \mu\text{m}$. Shown in Figure 4b is an AFM height image after removal of the PMMA layer by rinsing with acetic acid. Rather than columns, however, the AFM image shows that the features are holes penetrating through the PS film. This results, primarily, from the thickness of the individual layers. Here, the underlying PS layer was much thicker than the PMMA overlayer. Consequently, in this case, PMMA columns form within the PS layer. From equation (1) $\lambda=2.8 \mu\text{m}$ which is in good agreement with the value determined experimentally.⁴

The characteristic wavelength, λ , of fluctuations at the interface that are amplified by the applied electric field depends upon the sample geometry, the applied field and the dielectric constants of the materials. These parameters are explicitly shown in equation (1). We can define a reference wavelength and electric field as follows:

$$\lambda_0 = \frac{\epsilon_0 U^2 (\epsilon_1 - \epsilon_2)^2}{\gamma_{12} (\epsilon_1 \epsilon_2)^{1/2}} \quad (2)$$

and

$$E_0 = \frac{U}{\lambda_0} \quad (3)$$

Using these we can define a reduced wavelength and field by dividing λ and E by λ_0 and E_0 , respectively. For the reduced wavelength we have:

$$\frac{\lambda}{\lambda_0} = 2\pi \left(\frac{E_1 E_2}{E_0^2} \right)^{-3/4} \quad (4)$$

where E_1 and E_2 are the electric field strengths in layer 1 and 2, respectively. By replacing ϵ_1 with 1.0,

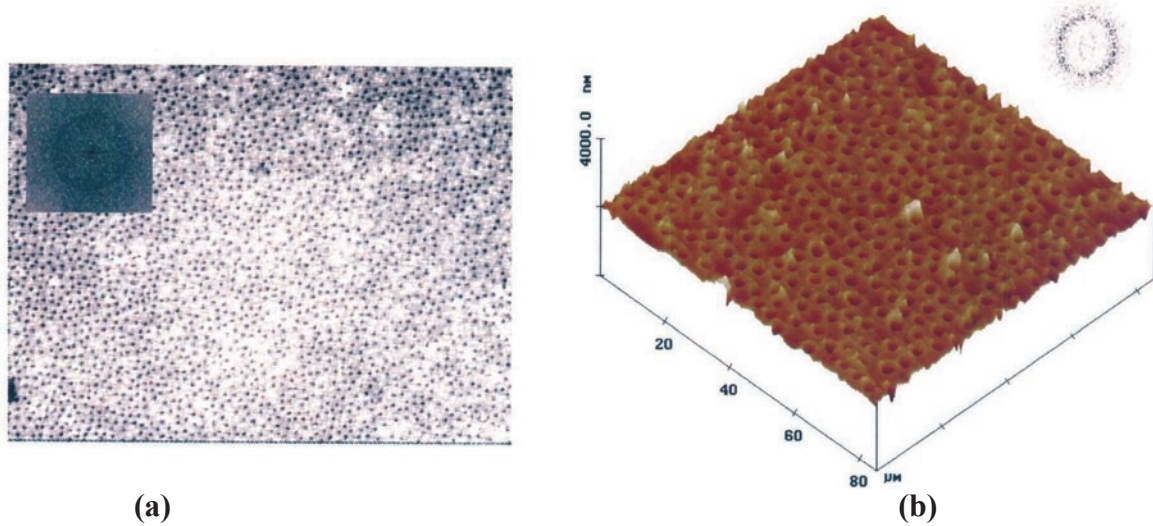


Figure 4. (a) An optical microscope image of PS/PMMA bilayer after removing the upper PMMA layer with acetic acid. The bilayer system held under 30V at 170°C for one day. The image size is 266x199 μm^2 . The initial film thickness of PS and PMMA were 730 and 290nm, respectively. The inset shows the 2D fast Fourier transform (FFT) pattern of the corresponding optical micrographs. (b) An AFM height image of the bilayer after removal of the upper PMMA layer. The 2D FFT of the AFM image is shown in the inset.

E_2 with E_p , the dimensionless variables, can be reduced to the polymer thin film case investigated by Schäffer et al.²

A master curve where the reduced wavelength λ/λ_0 is plotted as a function of the reduced field strength $\frac{E_1 E_2}{E_0^2}$ is shown in Figure 5. Shown are experimental data obtained from different experiments where the geometry of the system, the field strengths and the polymers have been varied. In addition, data from previous experiments on single polymer layers are included. The solid line in the figure is the theoretical reduced wavelength as a function of the reduced field strength using no adjustable parameters. As can be seen, there is excellent agreement between experiment and theory over four orders of magnitude in the reduced wavelength and reduced field strength.⁴

The derivation of equation (1) uses a linear approximation in treating the amplitude of fluctuations at the interface. Consequently, equation (1) should only be valid at the early stages of fluctuation growth and not, necessarily, at the latter stages of the process which includes the results shown here. Shown in Figure 6 are

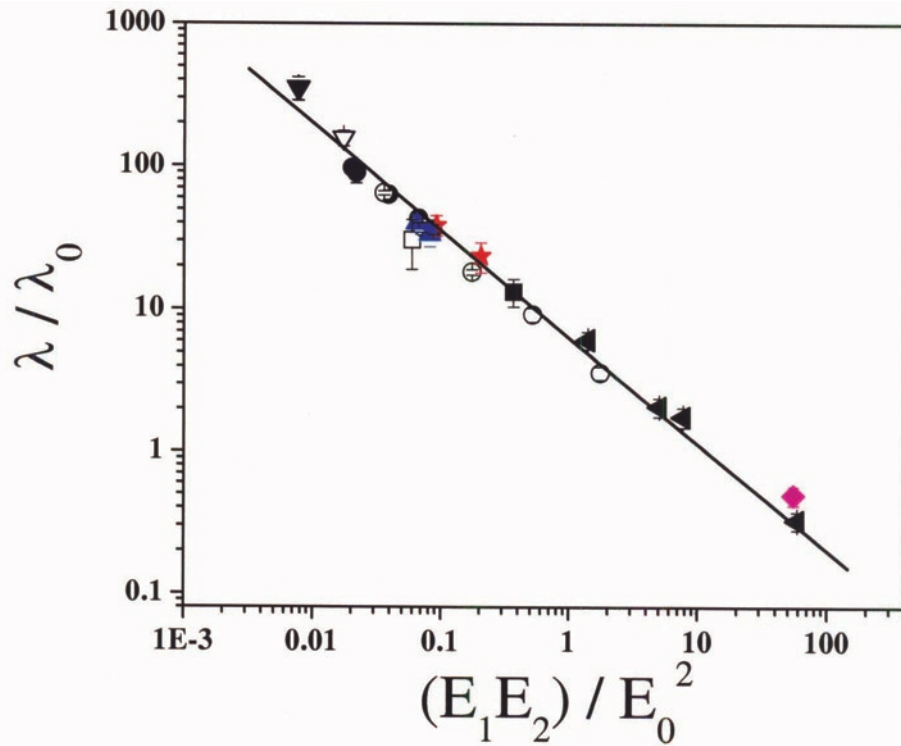


Figure 5. The master curve of the typical distance λ in varieties of thin film and bilayer experiments as a function of the electric field strength in the layer 1 and layer 2. The different symbols corresponded to ten data sets: $\blacklozenge$ PS/PMMA bilayer with $h_{PS} = 730\text{nm}$, $(d-h_{PS})_{PMMA} = 290\text{nm}$, $U=30\text{V}$; $\blacktriangledown$ PMMA/PDMS bilayer with $h_{PMMA} = 180\text{-}290\text{nm}$, $(d-h_{PMMA})_{PDMS} = 690\text{-}1030\text{nm}$, $U=19\text{-}50\text{V}$; $\star$ PS/PDMS bilayer with $h_{PS} = 305\text{nm}$, $(d-h_{PS})_{PDMS} = 400\text{nm}$ and 720nm respectively, $U=50\text{V}$; $\blacktriangle$ PS/PDMS bilayer with $h_{PS} = 550\text{nm}$, $(d-h_{PS})_{PDMS} = 570\text{nm}$ and 700nm respectively, $U=50\text{V}$; $\circ$ PSBr/air single layer with $h_{PSBr} = 740\text{nm}$, $d = 1.66\text{-}1.98\mu\text{m}$, $U=20\text{-}60\text{V}$; $\bullet$ dPS/air single layer with $h_{dPS} = 530\text{nm}$, $d = 1.06\text{-}1.85\mu\text{m}$, $U=30\text{V}$; $\blacktriangledown$, ∇ , $\blacksquare$ and $\square$ were the measurements from reference 3, which corresponded to PI/air thin film, PI/ODMS bilayer, OS/air thin film and OS/ODMS bilayer systems respectively. The straight line was calculated based on the eq (4) with a slope of $-3/4$.

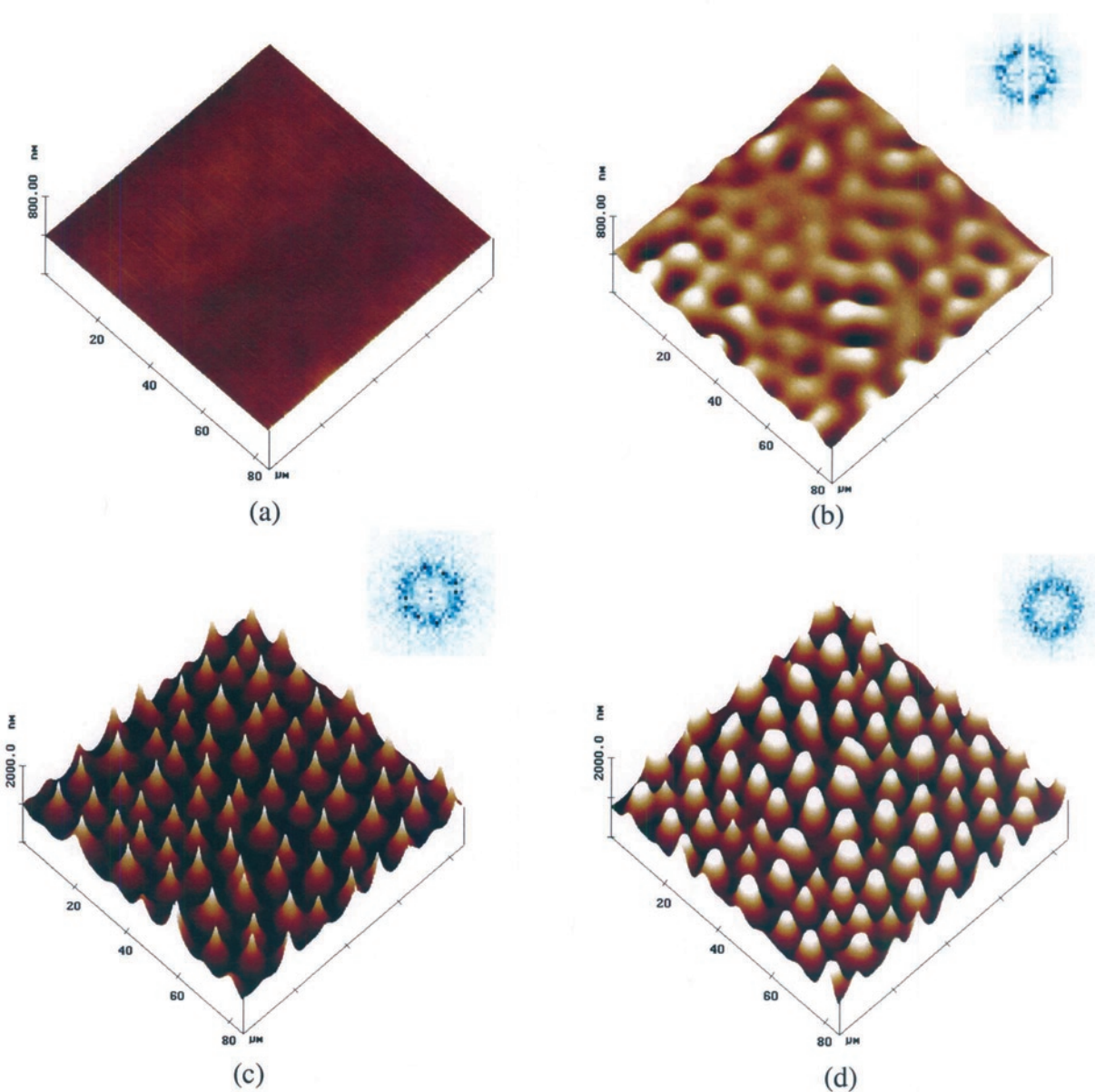


Figure 6. A series of AFM height images as a function of time of a PMMA/PDMS bilayer after removal of the PDMS layer ($h_{\text{PMMA}} = 220\text{nm}$, $h_{\text{PDMS}} = 890\text{nm}$) with 19V applied with heptane. The insets show a FFT of the images. The time sequence of the images correspond to the (a) initial interface, (b) initial stages of fluctuation growth, (c) amplification of fluctuations, and (d) the impingement of PMMA columns on the upper electrode.

a series of AFM height images characterizing the development of structure at the interface of a PMMA/PDMS bilayer with 19V applied at 170°C at different times. Each of the images was obtained on different bilayer samples where the upper PDMS layer was removed with heptane. Figure 6a shows that the initial interface was featureless. With time, fluctuations having a well-defined lateral wavelength are seen to emerge (Figure 6b). The 2D FFT of this image, shown in the inset, exhibits a maximum characteristic of a wavelength or average center-to-center distance of $10.5\ \mu\text{m}$. As time progresses, the amplitude of the fluctuations increases, the fluctuations become sharper and well-defined and begin to show a lateral order,

and instabilities that give rise to the formation of columns appear (Figure 6c). The 2D FFT of this AFM image, shown in the inset, exhibits a maximum corresponding to an average center-to-center distance of $10.5\ \mu\text{m}$, the same spacing seen at earlier times. The surface of the PMMA after the formation of PMMA columns that extend to the upper electrode is shown in Figure 6d. Contact with the upper electrode is evidenced by the flattened top of the columns and a well-defined lateral ordering is evident. The 2D FFT shown in the inset exhibits a maximum corresponding to a center-to-center distance between adjacent columns of $10.5\ \mu\text{m}$, the same as that seen at earlier times. The preservation of the characteristic distance throughout the growth of the columns justifies the comparison of the results obtained at later times to the linearized theoretical predictions. However, this does not hold true for the characteristic times describing the kinetic growth of these structures. As discussed earlier, discrepancies between the predicted times and those observed, based on the late stages of growth, are seen due to our inability to characterize the kinetics of the growth quantitatively³. These studies are currently in progress using fluorescent confocal microscopy.

The quantitative agreement between experiment and theoretical predictions in the master curve of Figure 5 shows that by controlling the sample geometry, the applied field or the interfacial energy, the size scale of the fluctuations can be controlled or manipulated. For a given geometry, polymer pair and field strength, reducing the interfacial tension provides a route to decrease the size scale of the fluctuations. Smaller size scale fluctuations that produce a larger interfacial area, can be amplified if the interfacial tension is reduced. It is well known that the addition of block copolymers that segregate to the polymer/polymer interfaces reduces the interfacial tension and, hence, provides an easy route towards structures that are hundreds to tens of nanometers in size. In the case of thin polymer films, a surface active agent should cause a similar effect. With fixed interfacial energies, increasing the electric field provides the easiest route to control the lateral length scales of the fluctuations. By combining both these effects the characteristic lateral length scale of the fluctuations can easily be placed in the nanoscopic level. Studies are in progress to systematically vary the concentration of the copolymer at the interface so as to develop a protocol for controlling the lateral dimensions quantitatively.

External electric fields were also used to amplify interfacial fluctuations in the air/liquid 1/liquid 2 system where one polymer dewets the other.⁵ Two different hydrodynamic regimes were found as a function of electric field strength. If heterogeneous nucleation leads to the formation of holes before the electrostatically driven instability sets in, the dewetting kinetics is not influenced by the electric field. Stronger electric fields lead to a spinodal electrohydrodynamic instability which causes the formation of polymer columns on top of the second polymer. The rapid column formation leads to a substantial deformation of the lower polymer layer at the column contact line, caused by the high viscous stress concentration there.

The sample setup of the air/PS/PMMA trilayer is shown in Figure 7. Rather than carrying out a time series with a constant applied field (which limits us to an optical investigation of the sample only), the use of a wedge geometry is an alternative way to observe (in a quasi static manner) the way how the instability forms with time, since the onset of the instability scales with the sixth power of the electric field in the polymer film.² Several different instabilities of the liquid 1 layer can be observed on the same sample:⁵ (1). For very large electrode spacings, the double film was predominately stable, except for isolated dewetting holes. (2). For intermediate electrode spacings, an undulatory instability of the liquid 1 surface with a characteristic wavelength is observed (see Figure 8, bottom left). (3). At small enough electrode spacings, an electrohydrodynamic instability caused the formation of liquid columns. This instability is accompanied

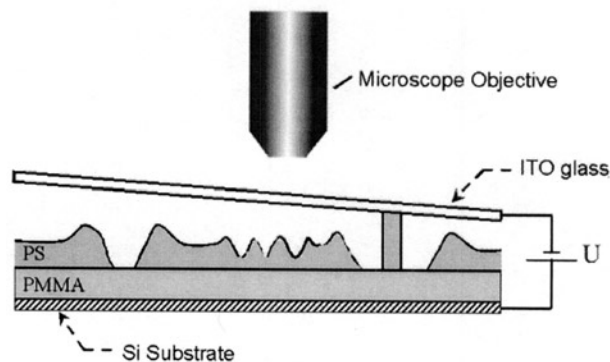


Figure 7. Typical sample configuration in the study. The air / Polystyrene(PS) / Poly(methyl methacrylate) (PMMA) system was sandwiched between a highly polished and doped silicon wafer (lower electrode) and an ITO microscope slide (upper electrode). The distance between the two electrodes was controlled by evaporating SiO_x as a spacer (at the edges of the slides on top of the ITO). Typically, the electrode spacing varied by a few micrometers over a lateral distance of approx. 1cm. The structure formations of the system under an applied electric field (0V, 30V and 60V) were studied by optical microscopy in the reflectance mode. After removal of the top electrode, the sample was imaged by atomic force microscopy.

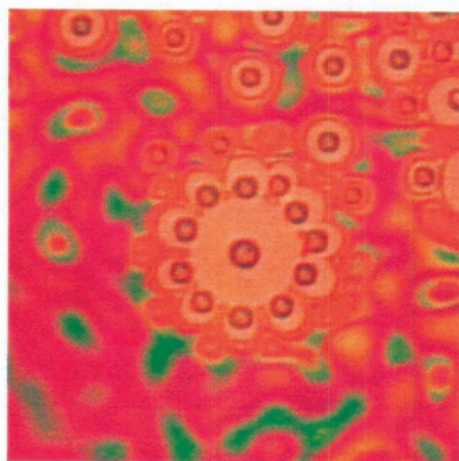


Figure 8. An optical microscope image of air/PS-96k /PMMA-95k trilayer with 30V applied in the configuration shown in Figure 7. The image size was $212 \times 212 \mu\text{m}^2$.

by the dewetting of PS on top of PMMA. Both, the nucleated and spinodal instabilities are observed (see Figure 8 center and top right, respectively). The structure in the center of the micrograph consists of an initial column (primary cylinder) that was heterogeneously nucleated earlier in the experiment. As the dewetting rim grew in size and height, fluctuations with a characteristic spacing were amplified and grew into regularly spaced columns (secondary cylinders). Each secondary column was then surrounded by its own dewetting zone. As PS dewets the PMMA, PS accumulates in the dewetting rim, changing the position of the PS/air interface locally. This creates an instability along the rim which, in turn leads to the formation of secondary cylinders. Similar to the nucleated instability, the columns formed by a spinodal process (Figure 8 top right) are each surrounded by a dewetting zone.

The extent of the deformation of the PMMA/PS interface in the vicinity of the 3-phase contact line can be characterized by the height h , i.e. peak to baseline distance. Shown in Figure 9 is the height of the deformation of the primary cylinder at the PMMA/PS interface under the PS columns as a function of the ratio of PS and PMMA molecular weights. As seen, as this ratio increase or as the mobility of PMMA increases in comparison to that of PS, the extent of deformation at the PMMA/PS interface increases. In addition, for a given ratio of molecular weights, as the applied field strength increases by increasing the applied voltage while keeping the separation distance, d , between two electrodes, or by decreasing d while keeping the applied voltage (inset in Figure 9), the magnitude of the deformation increases.

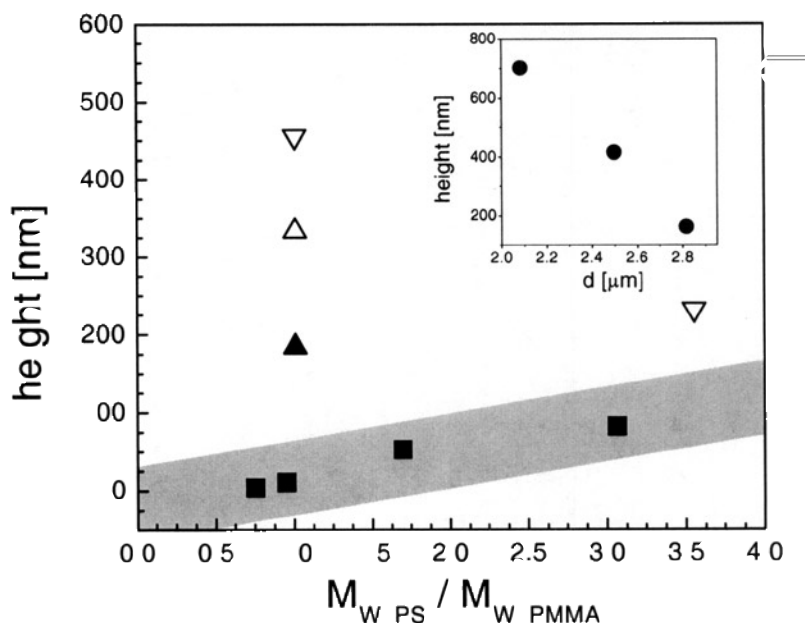


Figure 9. Deformation of height under the dewetting rim as a function of the ratio of the molecular weights of the PS and PMMA from Lambooy et al.⁶ (black squares) and our experiments (gray area). The triangles are the deformations observed for the PMMA-95k/PS-96k system with 30V applied ($\blacktriangle$: sample 2, $\triangle$: sample 4) and the inverted triangles were obtained with 60V applied for PMMA-95k/PS-96k (sample 3) and PMMA-27k/PS-96k (sample 9). The inset shows the deformation of height as a function of separation distance of the electrodes, d , for the PMMA-95k/PS-96k bilayer at 60V applied field (samples 5, 6, 7). The detailed information is given in ref. 5.

Rather than sandwiching the polymer thin film in between two infinite long electrodes, applying the pattern electrodes would introduce a local enhancement of the applied field. The evolution of surface instabilities under finite size upper electrode leading to the pattern formation and selection in the electric field is being investigated. Figure 10 shows the experimental configuration in the study. The stripe-like Cr/Au electrodes are infinitely long in x , but with a finite width in y . A real time study of 340nm PI thin film under 50 μ m Au/Cr electrode with 15V applied is shown in Figure 11.

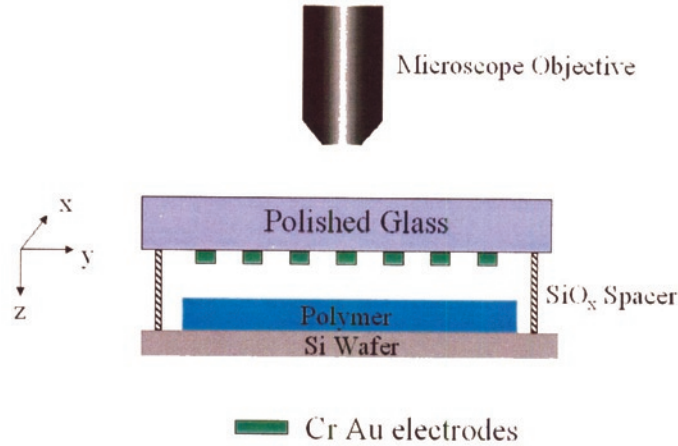


Figure 10. Sketch of the sample configuration in the study. Either periodic or gradient Au/Cr electrodes with finite width in y can be prepared by electric beam lithography.

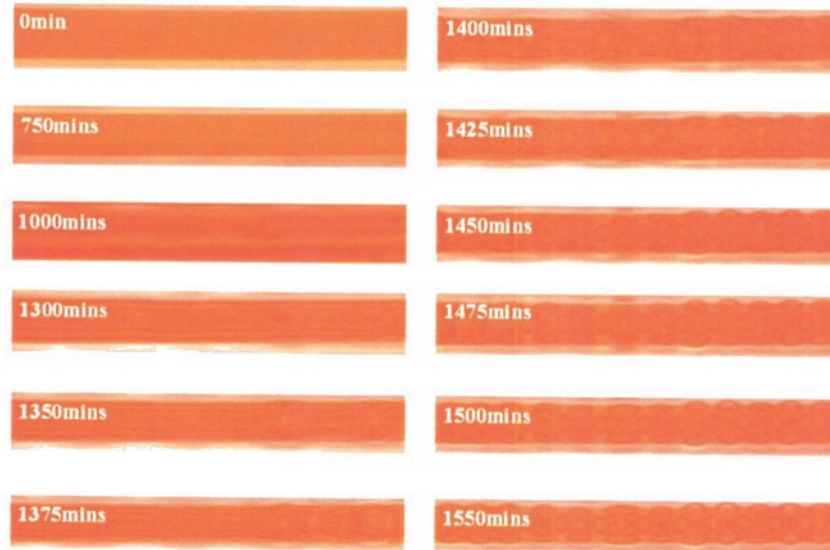


Figure 11. Spatio-temporal evolution of 340nm PI thin film under 50 μ m Au/Cr stripe with 15V applied.

The buildup of instability is clearly evident around 1000mins. With time the amplitude of fluctuation is enhanced, the formation of PI columns, which bridge between two electrodes, can be seen in 1350mins. As time progresses, more columns are formed and the characteristic wavelength of 40 μ m with an average diameter of 17 μ m is established eventually. Experiments are being performed as a function of the film thickness, the applied field, the width and the shape of the pattern electrodes to quantify the confinement effect imposed by the finite size upper electrode.

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EFFECT OF GRAVITY LEVEL ON THE PARTICLE SHAPE AND SIZE DURING ZEOLITE CRYSTAL GROWTH

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Abstract

A microscopic diffusion model is developed to represent solute transport in the boundary layer of a growing zeolite crystal. This model is used to describe the effect of gravity on particle shape and solute distribution. Particle dynamics and crystal growth kinetics serve as the boundary conditions of flow and convection-diffusion equations. A statistical rate theory is used to obtain the rate of solute transport across the growing interface, which is expressed in terms of concentration and velocity of solute species. Microgravity can significantly decrease the solute velocity across the growing interface compared to its earth-based counterpart. The extent of this reduction highly depends on solute diffusion constant in solution. Under gravity, the flow towards the crystal enhances solute transport rate across the growing interface while the flow away from crystals reduces this rate, suggesting a non-uniform growth rate and thus an elliptic final shape. However, microgravity can significantly reduce the influence of flow and obtain a final product with perfect spherical shape. The model predictions compare favorably with the data of space experiment of zeolites grown in space.

Introduction

The growth of crystals in microgravity has been a potentially attractive means of producing large crystals. This has been attributed to the reduction of density-driven convection and suspension of growing crystals in the nutrient pool¹⁻³. It is generally believed that convection at the interface of the growing particle plays a significant role in determining the growth rate and the final shape of crystals. In the presence of gravity, the density-driven convection that arises from the density difference between the fluid in the depletion zone and that in the bulk, and the forced convection that arises from particle sedimentation during crystal growth from solution affect solute transport across the growing interface and, in turn, the particle shape⁴. In particular, flow towards the crystal enhances the solute transport rate across the growing interface while the flow away from crystal reduces this rate, suggesting a non-uniform growth and an elliptic crystal shape. Microgravity in an orbiting spacecraft could help isolate the effects of natural convection and minimize sedimentation⁵. This is expected to promote larger perfect crystals by reducing the convection and allowing a longer residence time in a high-concentration nutrient field. Although this size increase and shape optimization in microgravity have been observed, our understanding of the underlying mechanism of the influence of variable gravity on solute transport and particle shape is still rather limited. The objective of this paper is to develop a theoretical model to quantify these relationships.

Zeolite crystal growth is a process of transporting solute species from the solution to the crystal surface and then incorporating them into the crystal surface at the kink⁶. As a crystal grows from the solution, it depletes the solute species, producing a concentration-depleted zone around it. In this region, the solute concentration

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changes continuously from the value at the crystal surface to that in the bulk solution. The concentration profile in the depletion zone varies with time as the crystal grows and is controlled by the balance between the flow of solute species towards the crystal surface and the rate of incorporation of these solutes into the crystal lattice. The kinetics of incorporation at the surface is linked to the bond configuration of the crystallographic structure, while the flow towards the surface is highly dependent on the mass transport properties in the bulk solution, which turn out to be crucial for the overall crystal-growth process. The diffusive transport through the depletion zone around a growing crystal is therefore responsible for any observable difference between on-ground and microgravity experiments including crystal quality enhancement.

Although a number of experiments have been performed on crystal growth and shape evolution both under gravity and microgravity, there is no theoretical model to describe particle shape evolution and kinetics of mass transport in the boundary layer of a growing crystal. Carotenuto et al.⁷ performed an order-of magnitude analysis of natural convection during solidification and crystallization in microgravity. This model however does not account for the motion of the crystal and the kinetics of mass transport. The shape evolution as the crystal grows under microgravity is also not addressed.

A model is developed to describe the crystal growth and shape evolution by integrating particle dynamics with the convection-diffusion equation in the boundary layer around the growing crystal. Specifically, particle dynamics is used to obtain the drag force and relative velocity between the particle and the solution, while the convective diffusion equation is used to describe the solute distribution and thus the mass flux across the growing interface. Equally important is studying the impact of variable gravity on evolution of particle shape both on ground and in microgravity. The model is validated by comparison of its predictions with a recent set of experimental data on zeolite crystal growth.

Formulation

Particle Dynamics

We consider a spherical crystal particle growing in an incompressible solution. As shown in Fig.1, the crystal falls down in the presence of gravity due to the difference in density. A boundary layer thus develops around the particle with different solute concentration from the bulk. The integro-differential equation governing the motion of the growing crystal can be expressed as⁸:

$$m_p \frac{dV_p}{dt} = (m_p - m_f)g + F \quad (1)$$

where V_p is the velocity of the particle, m_p is the mass of the particle, m_f is the fluid mass which has the same volume as particle, g is the gravity, and F is the hydrodynamic force associated with the fluid movement. Typically, the first term on the right side of Eq.(1) represents the buoyancy force and the second results from the fluid motion about the particle. For the viscous low Reynolds number flow, the hydrodynamic force can be expressed as⁹:

$$F = 6\pi\mu R V_p. \quad (2)$$

where μ is the viscosity and R is the radius of the particle.

Typically, once nucleated in solution, the crystal will accelerate until it reaches a terminal velocity in the presence of the gravity. The acceleration time and the terminal velocity are strongly dependent on the particle size R , the density ratio of particle to solution δ , and the viscosity of solution μ . For an unbound solution at rest, the acceleration time of a spherical particle can be expressed by¹⁰:

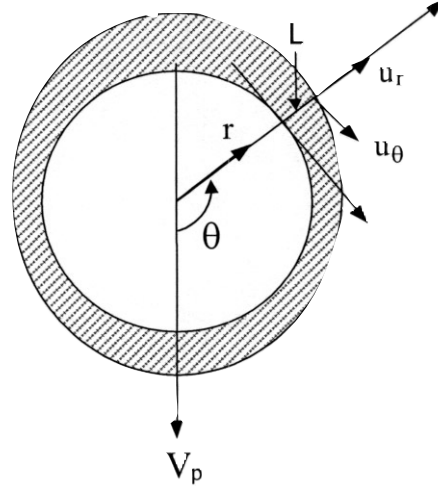


Figure 1. Schematic of the boundary layer or depletion zone around the crystal.

$$\tau_{acc} = \frac{2}{9} \frac{\rho \delta}{\mu} R^2 \quad (3)$$

and the terminal velocity of particle can be expressed by

$$V_p = \frac{2}{9} \frac{\rho g (\delta - 1)}{\mu} R^2 \quad (4)$$

where ρ is the density of the solution. For zeolite particles with a size in the range 0.01-10 μm settling in a solution with a viscosity of $10^{-3} \text{ kg/m}\cdot\text{s}$ under gravity of 9.81 m/s^2 , the particle acceleration time will be in the range $4.4 \times 10^{-11} \sim 10^{-5}$ seconds. Therefore, it is reasonable to assume that the growing crystal will fall at a steady state.

Governing Equation for Flow in the Boundary Layer

Within this framework, the governing equations for continuity, Navier-Stokes, and convection-diffusion of solute species in the boundary layer of growing crystal can be expressed as¹¹:

$$\nabla \cdot \mathbf{u} = 0 \quad (5)$$

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u} + \mathbf{g} \quad (6)$$

$$\frac{\partial c}{\partial t} + (\mathbf{u} \cdot \nabla) c = D \nabla^2 c \quad (7)$$

where $\mathbf{u}$ is the velocity of fluid, p is the pressure, t is time, c is the concentration of the solute species, and D is its diffusivity and ν is the kinematic viscosity of solution. We impose the Boussinesq-Oberbeck approximation in which physical parameters are assumed constant everywhere but in the momentum generation term of the equations above.

This approach amounts to assuming the bulk acts as a nutrient pool for the crystal. When r approaches infinity, the velocity of solution reaches the terminal velocity of particle and the solute concentration is assumed to be a constant c_b . The boundary for the convection-diffusion equation is expressed using the transport rate of solute across the interface between the crystal and the solution thus:

$$J = -D \left(\frac{\partial c}{\partial r} \right)_{r=R} . \quad (8)$$

The kinetics of crystal growth dictates that this flux is related to the solute supersaturation as¹²:

$$-D \left(\frac{dc}{dr} \right)_{r=R} = K_e \left(\frac{c_i}{c_s} - \frac{c_s}{c_i} \right) . \quad (9)$$

where c_i is the solute concentration at the interface, c_s is the equilibrium concentration and K_e is the equilibrium exchange rate between the solution and crystals. The equilibrium exchange rate can be expressed as a combination of two terms¹², thus:

$$K_e = K_r c_s \sqrt{T} - K_c c_s u_r(L) \quad (10)$$

where T is the temperature, $u_r(L)$ is the radial velocity of solute molecules at the edge of the boundary layer whose thickness is L , and K_r and K_c are two empirical constants. The first term of Eq.(10) is the rate that would exist if the solution were static, and the second term results from the convection due to the sedimentation of growing crystals.

We assume the concentration in the bulk is constant throughout the growth process. Thus, the portion of solution outside of the diffusion layer is approximated as a reservoir that has a given concentration. Since the concentration in the bulk is assumed unchanged by the growth process, strictly speaking the system cannot reach equilibrium.

Crystal Growth and Morphology

The morphology of the crystal strongly depends on the growth rates of the different crystallographic faces. According to Bravais rule, the important faces governing the crystal morphology are those with the highest reticular densities and the greatest interplanar distances. Or, in simpler terms, the slowest-growing and most influential faces are the closed-packed and have the lowest Miller indices. The growth of a given face is typically governed by the crystal structure and defects on the one hand, and by the environmental conditions especially the flow on the other. A reasonable evolution of the crystal size can therefore be written as a function of solute molecule flux across the growing interface, thus:

$$\frac{dR}{dt} = \frac{J}{\rho_c} \quad (11)$$

where ρ_c is the crystal density.

A change in the flow environment can influence the shape of the growing crystal. Due to the symmetry, we consider the shape change along the principal axis in the plane of gravity such that a two-dimensional shape is considered as shown in Fig.1. Therefore, the ratio η of the minor axis (gravity direction) to the major axis (sectional) can be used to describe the evolution of shape of elliptic crystal as it grows, thus:

$$\eta = \frac{R_{\parallel}}{R_{\perp}} \quad (12)$$

where $R_{\parallel}$ and $R_{\perp}$ are the radii of the growing crystal in the gravitational and sectional directions, respectively. Numerically, this ratio equals one when the crystal is spherical.

Computational Details

The equations governing the flow and solute transport are solved with the SIMPLEC algorithm embodied in the CFD-ACE software code. This code uses a control volume based finite difference formulation with upwind difference for convective fluxes.

Having discussed the crystal growth from solution, we shift our attention on the boundary layer around the crystal. We will present a dynamic simulation of crystal growth. To handle this simulation, a structured multiblock scheme is developed with multizone adaptive grid generation (MAGG) algorithm to avoid the stretching and compression of grids. The crystal growth system can be divided onto three blocks: crystal, boundary and bulk block. The grids in each block can be generated and moved adaptively independent of other blocks. The crystal block becomes larger and the bulk becomes small as the crystal surface moves outward. The efficiency and accuracy of the dynamic simulation of crystal growth can be improved by using this algorithm. The values of the principal input parameters used in the computation are presented in Table 1.

Table 1. Parameter values used in calculations.

Parameter	Value
Kinematic viscosity ν (m ² /s)	1.12×10^{-6}
Solution density ρ (kg/m ³)	1×10^3
Crystal density ρ_c (kg/m ³)	2×10^3
K_r (m/sK ^{1/2})	6×10^{-11}
K_c	3×10^{-9}

Results and Discussion

Figure 2 shows the solute velocity across the crystal surface as a function of gravity level and solute concentration ratio at interface to bulk for solute diffusion constant (a) 1.0×10^{-5} m²/s, (b) 1.0×10^{-7} m²/s and (c) 1.0×10^{-9} m²/s, respectively. It is seen that the solute velocity decreases as the gravity level decreases and the solute concentration ratio at the interface to the bulk increases. At high diffusion constant as shown in Fig. 2a, variable gravity does not affect the solute flux. However, for a low diffusion constant as shown in Fig. 2b and 2c, microgravity can decrease the solute flux to 20% and 70 % of ground value, respectively. This is due to the fact that the solute transport is mainly controlled by diffusion at high diffusion constant while the convection-controlled transport can compete to the diffusion-controlled transport at a low diffusion constant. In addition, for three diffusion constants tested, gravity levels in the range of 1.0×10^{-2} - 10^{-5} m/s² have no significant effect on solute flux. There are several solute species involved in zeolite crystal growth from solution. The diffusion constants of these species are typically in the range of 10^{-5} - 10^{-12} m²/s. As the gravity level decreases, the transport of solute species with low diffusion constants will play a more significant role in crystal growth.

Two cases are considered for crystal growth dictated by the type of boundary conditions on solute transport. The first assumes a fixed relative solute concentration at the growing interface. This case corresponds to a system in which crystal growth process locks the solute concentration at a fixed value at the growing interface. The predicted results are presented in Fig. 3 to 5. The second uses the boundary conditions expressed in Eqs.(9) and (10) where the parameters are presented in Table 1. This condition implies a diffusion-controlled mechanism of crystal growth. The predicted results are presented in Fig.6 to 8.

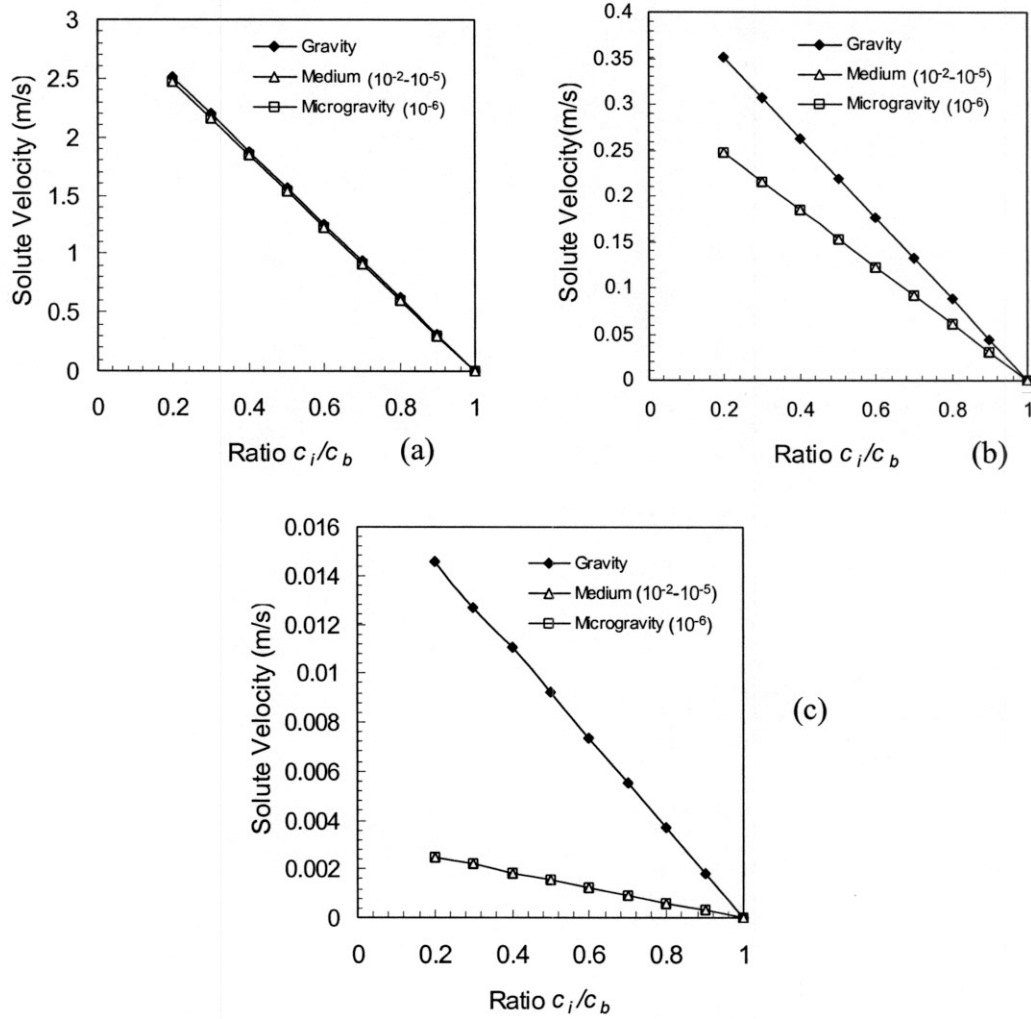


Figure 2. Solute velocity across the growing interface as a function of concentration ratio and gravity level for solute diffusion constant (a) $1.0 \times 10^{-5} \text{ m}^2/\text{s}$, (b) $1.0 \times 10^{-7} \text{ m}^2/\text{s}$ and (c) $1.0 \times 10^{-9} \text{ m}^2/\text{s}$.

Figure 3 shows the evolution of particle shape and solute concentration profile as the crystal grows on ground (a) and in microgravity (b). Buoyancy-induced convection dominates solute transport around the crystal on the ground and induces a thinner concentration-depletion boundary layer around the crystal than in microgravity. On the other hand, mass transport is governed by diffusion in microgravity producing a thicker depletion zone where the concentration gradient is considerably lower than on earth. More importantly, density-driven convection under gravity produces a solute-poor region on the upper position of the crystal. In this region, the flow away from the crystal reduces the frequency with which the solute species collide with the crystal surface. Coupled with the low solute concentration gradient close to the crystal surface, growth in this part is considerably slower than other regions around the crystal.

Figure 4 shows the crystal growth rate in the three directions on the ground (a) and in microgravity (b). The overall growth rate decrease as the crystal grows in both cases. This is due to the progressive decrease in solute concentration gradient close to the crystal surface. The growth rate in microgravity is lower than that on ground by one order of magnitude, consistent with space experiments on zeolite crystal growth. There are significant differences in the growth rate in the three directions on ground. The growth rate in the

direction $\theta = 180^\circ$ is nearly four times that for $\theta = 0$ because of density-induced convection. The difference in the growth rate between the directions is insignificant in microgravity, as would be expected.

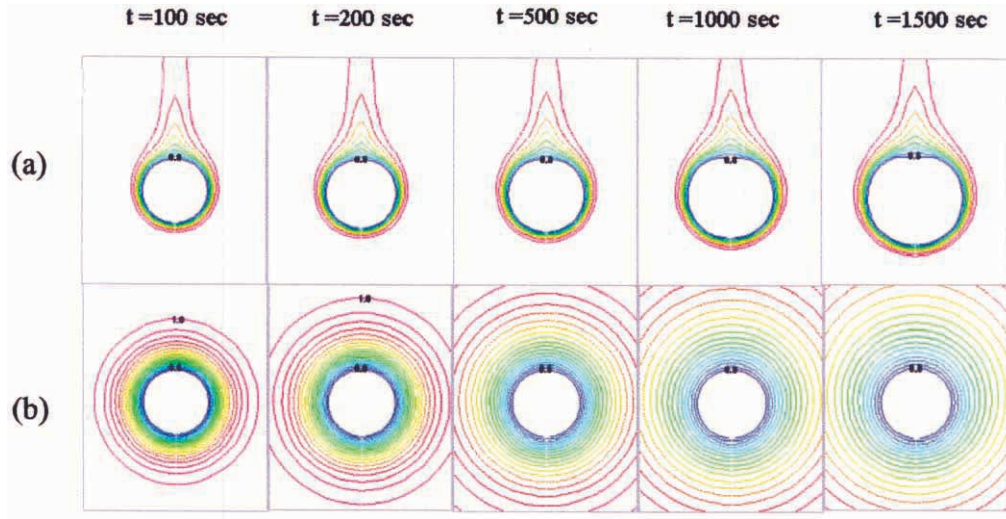


Figure 3. The evolution of particle shape and solute as the crystal grows with a fixed solute concentration ratio of interface to bulk for (a) gravity (9.80) and (b) microgravity (10^{-6}).

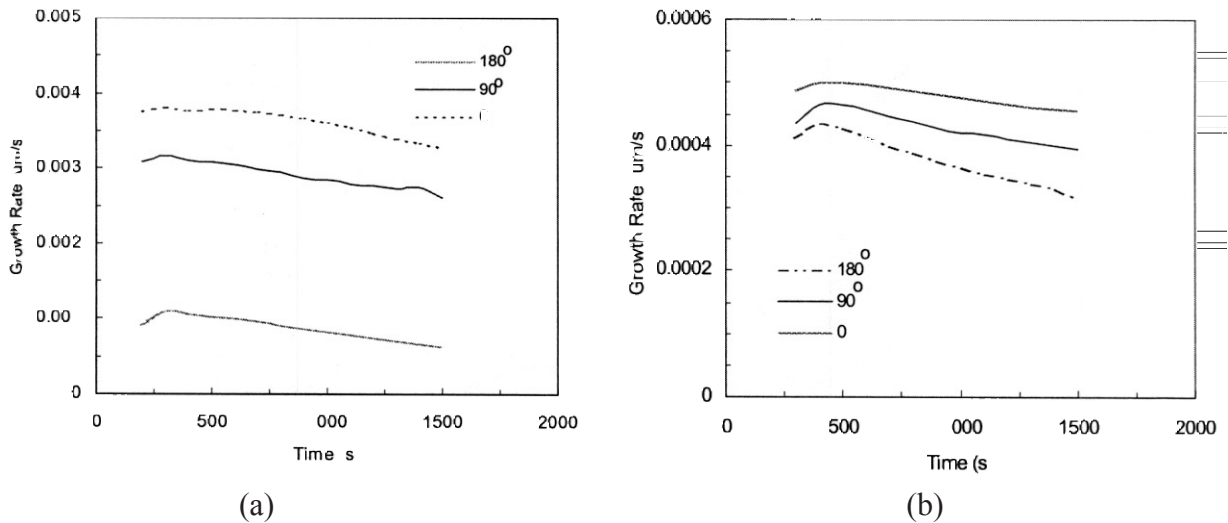


Figure 4. The crystal growth rate in three directions (θ) with a fixed solute concentration ratio of interface to bulk for (a) gravity (9.80) and (b) microgravity (10^{-6}).

The evolution of shape parameter η as the crystal grows on ground and in microgravity is presented in Fig. 5. The curve for $\eta = 1$ representing a spherical shape is also presented for comparison. The crystal that grows in microgravity keeps the spherical shape while the crystals grown on the ground would be predicted to evolve into an ellipsoid. This is largely due to non-uniform growth rate on the ground under the influence of density-driven convection while uniform growth rate is maintained in microgravity.

Figure 6 shows the evolution of particle shape and solute profiles as the crystal grows on the ground (a) and in microgravity (b). Buoyancy-induced convection deeply affects the solute transport in the boundary layer as the crystal falls down on ground. However, this influence is not significant due to the slow growth

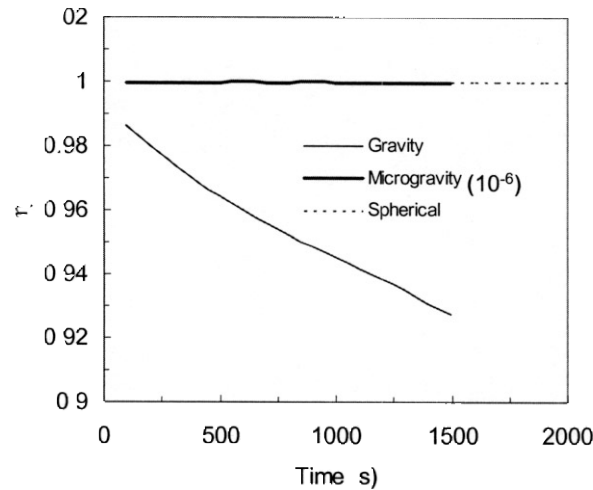


Figure 5. The evolution of parameter η as the crystal grows with a fixed solute concentration ratio of interface to bulk.

rate that is dependent on solute concentration near the crystal surface. Mass transport is governed by diffusion as the crystal grows in microgravity.

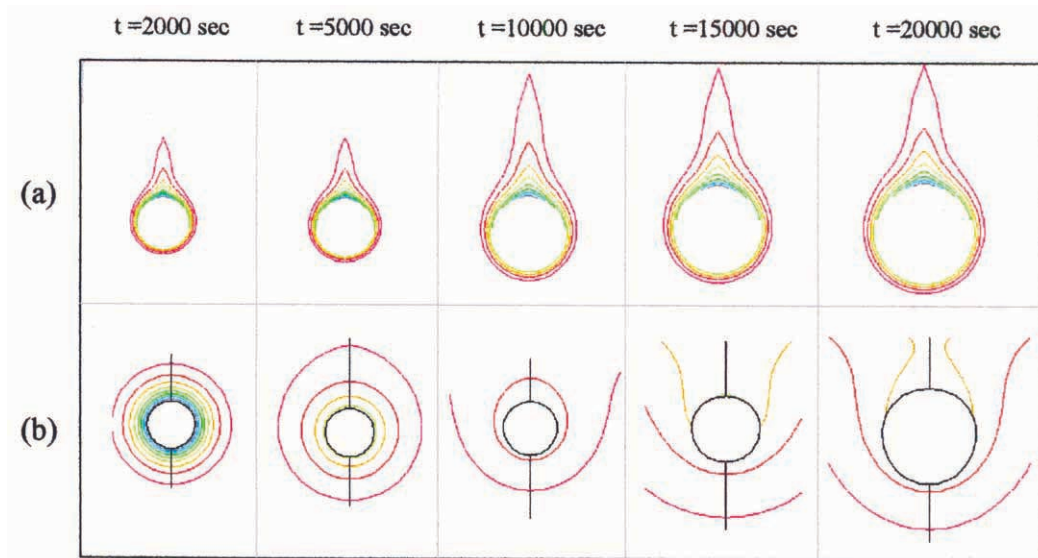


Figure 6. Evolution of particle shape and solute as the crystal grows with $K_I=6.0 \times 10^{-11}$ and $K_C=3.0 \times 10^{-9}$ and $T=100^\circ\text{C}$ for (a) gravity (9.80) and (b) microgravity (10^{-6}).

The growth rates of crystal as a function of θ and gravity level are presented in Fig. 7. The growth rate on the ground varies with θ since natural convection and diffusion jointly govern solute transport in the boundary layer. In microgravity, the variation of the growth rate with θ is relatively small due to the suppression of natural convection.

The evolution of shape parameter η as the crystal grows on ground and in microgravity is presented in Fig. 8. The variation of growth rate with θ results in an elliptic shape on ground and a nearly spherical shape in microgravity.

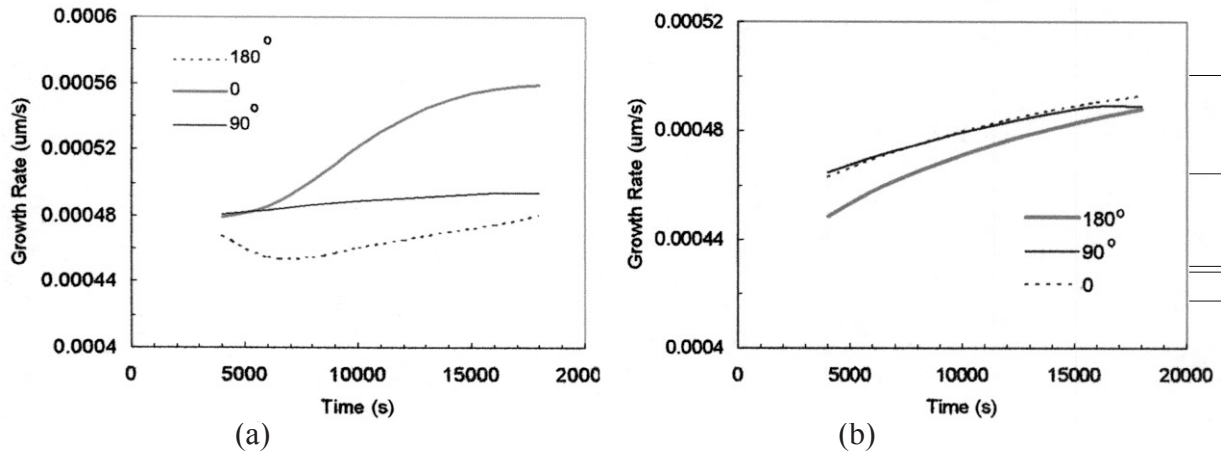


Figure 7. The crystal growth rate in three directions (θ) with $K_F = 6.0 \times 10^{-11}$ and $K_C = 3.0 \times 10^{-9}$ and $T = 100^\circ\text{C}$ for (a) gravity (9.80) and (b) microgravity (10^{-6}).

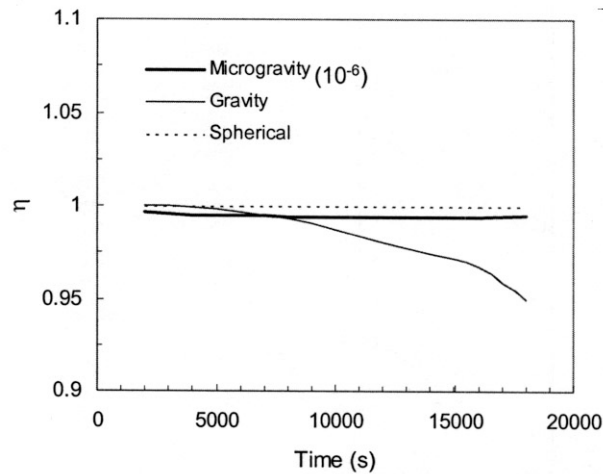


Figure 8. The evolution of parameter η as crystals grow with $K_F = 6.0 \times 10^{-11}$ and $K_C = 3.0 \times 10^{-9}$ and $T = 100^\circ\text{C}$ both on ground (9.80) and in microgravity (10^{-6}).

Conclusions

We developed a microscopic diffusion model for the solute transport in the boundary layer to describe the influence of gravity on crystal shape and solute distribution. The full particle dynamics and crystal growth kinetics are considered in expressing the boundary conditions for the governing equations. A statistical rate theory is used to obtain the rate of solute transport across the growing interface. The latter is expressed in terms of concentration and velocity of solute species. Microgravity can significantly decrease the solute velocity across the growing interface compared to its earth-based counterpart. The extent of this reduction highly depends on solute diffusion constant in solution. Under gravity, the flow towards the crystal enhances solute transport rate across the growing interface while the flow away from the crystal reduces this rate, suggesting a non-uniform growth rate and resulting in an elliptic final shape. Microgravity significantly suppresses the flow, giving a final product with spherical shape.

Acknowledgements

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NON-INTRUSIVE MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF LIQUIDS BY ELECTROSTATIC-ACOUSTIC HYBRID LEVITATION

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Abstract

In the current task, we have developed a novel technique that can be used to determine the viscosity and surface tension of highly viscous liquids levitated with an ultrasonic levitator. The technique involves levitation of a liquid drop and elongation by rotating the drop beyond the point of bifurcation. The elongated drop is then relaxed and allowed to restore itself to its original shape by surface tension. The time-dependent shape parameters of the relaxing drop are related to the viscosity through a relaxation model. The feasibility of the technique has been demonstrated by performing the measurement using sucrose solutions as a model liquid drop. The obtained viscosity values show a good correlation with those determined by a falling ball method, a proven technique. The ultrasonic levitator did not have capability to allow the variation of the temperature of the drop.

We have also developed a method that can be used to determine the thermal diffusivity coefficient of undercooled liquids. The technique involves levitation of a small amount of liquid in the shape of a flattened drop using an acoustic levitator and heating it with a laser beam. The heated drop is then allowed to cool naturally by heat loss from the surface. Due to acoustic streaming, the heat loss mainly occurs through the equatorial section of the drop. The measured cooling rate in combination with a radial heat condition model allows us to determine the thermal diffusivity coefficient of the drop. We demonstrated the feasibility of the technique using glycerin drops as a model liquid. The agreement between the experiment and the model turns out to be fair at best. The reason is mainly due to the inadequacies of the 1-D heat conduction model used, and other surface-loss approximations.

Thermocapillary flow measurements of drastically flattened drops have been initiated in the current task. The drastically flattened drop has flows that are dominated by thermocapillary forces because the buoyancy-driven flows are mitigated owing to the low hydrostatic head over the drop thickness. As a result, there is minimal interference from the natural convection, and with thermocapillary flow being isolated, some thermal properties can be inferred from the measurements. We have demonstrated the technique using a glycerin drop that is acoustically levitated and flattened using an acoustic apparatus.

Theoretical analysis of streaming flows about liquid drops and solid particles have been carried out in connection with levitation. The present study deals with the steady streaming in the incompressible limit around a rigid oblate spheroid that performs translational oscillations relative to the fluid medium along its symmetry axis. Motivation for such a study is two-fold. On the one hand, liquid drops are known to be squeezed to an oblate shape, quite close to an oblate spheroid, when levitated in acoustic levitators at

Keywords: acoustic levitation, thermal diffusivity, viscosity measurement, streaming

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sufficiently high intensities of the sound field. Due to their large density and dynamic viscosity as compared to those of the surrounding air, the drops may behave to a high degree as rigid bodies streaming-wise. In particular, the influence of the acoustically induced internal circulation in a drop on the steady streaming in the air can be estimated. On the other hand, the study of the streaming around a body more complex than a sphere may also be important from an intrinsic standpoint, especially in view of our intention to consider the disk limit. The choice of the oblate spheroid for this purpose is convenient in view of the availability of the oblate spheroidal coordinate system.

1. Viscosity Measurement

We have developed a technique that can determine the viscosity of highly viscous liquids, particularly, undercooled liquids that exist at temperatures below their freezing points [2]. The technique involves levitation of a liquid drop using an ultrasonic standing wave, and elongation of the drop by rotating it beyond the bifurcation point. The elongated drop is then allowed to be restored to its original shape by the surface tension driven relaxation. The time-dependent shape parameters of the relaxing drop are related to the viscosity through a relaxation model. In addition, this technique can also determine the surface tension that has a known relationship with the angular velocity at the bifurcation point.

The experimental apparatus is schematically shown in Figure 1 and a typical sequence of the relaxation of a sucrose solution drop is shown in Figure 2. The ultrasonic driver is operated at approximately 18kHz and is

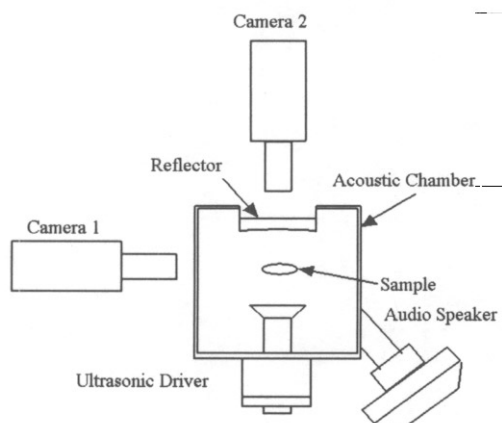


Figure 1. Schematic diagram of experimental apparatus showing the key parts.

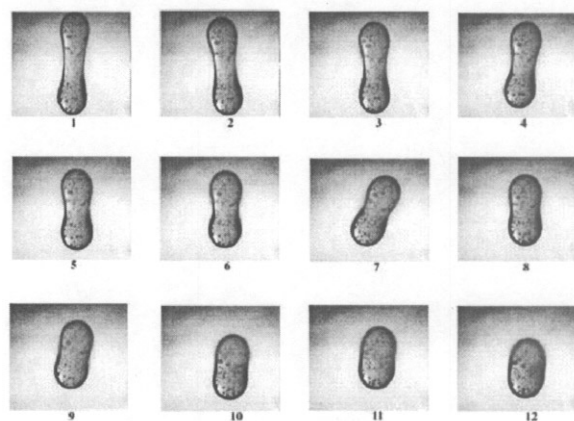


Figure 2. A sequence of the shape relaxation of the initially elongated drop with $\eta = 1.4 \times 10^3$ Poise at 28°C.

used to generate a vertical (z direction) standing wave between the driver head and the reflector for levitating a drop. Two broadband audio speakers (the second one is not shown) are placed at the bottom corners of the chamber and are facing each other at a 90° angle. The audio speakers are operated at approximately 1.4 kHz and are used to generate lateral standing waves (x and y directions) in the acoustic chamber. A proper torque is exerted on the drop when the relative phase of the lateral standing waves is adjusted. Two cameras are used to record the images of the levitated drop: Camera 1 is used to record the side view of the drop, which is generally deformed into an oblate spheroid due to the acoustic pressure. The images are used to determine the aspect ratio and the true volume of the drop. Camera 2 looks down the drop through the hole made on the reflector. This camera is capable of capturing the images up to 2000 frames per second and is used to record the top view of the rotating drop at the bifurcation point and during the shape relaxation. Although the apparatus does not have the capability of controlling the sample temperature, the temperature inside of the chamber remains between 28 and 29°C throughout the measurement. There is a size limitation on the drops to be levitated and elongated beyond the bifurcation point using this apparatus. As a result, we can only perform the measurement on the drops with $1.0 \text{ mm} < R_0 < 1.5 \text{ mm}$, where R_0 is the radius of the equivalent spherical drop whose volume is equal to that of the deformed drop.

We selected samples of sucrose (sugar) solution as a model liquid, mainly because their viscosities could be easily varied over many orders of magnitude at room temperature by adjusting the water content. A small amount of the solution was attached to the tip of a needle and inserted into the levitation chamber. The solution was gradually detached from the needle by gravity and acoustic radiation pressure, and shaped into a drop. Once the drop was completely detached, it was formed into an oblate spheroid due to the force balance among the surface tension, gravity and the acoustic forces. The levitation parameters were then adjusted so that the drop became stationary. The image of the stationary drop was digitally recorded for the volume determination. The audio speakers were then turned on to exert a torque on the drop. The drop started rotating and expanded laterally as the rotation rate increased. The high-speed camera continuously monitored the rotation of the drop and recorded the moment of bifurcation for the angular velocity determination. After bifurcation, the drop evolved into a two-lobed shape and continued to elongate until the torque was suddenly removed by turning off the audio speakers just before fission would occur. The elongated drop immediately started decelerating due to air drag and eventually stopped rotating. In order to shorten the deceleration stage, a counter torque was briefly applied by reversing the phase difference of the lateral standing waves before turning off the speakers in some cases.

The shape evolution of the drop during the deceleration and subsequent non-rotating stages was recorded for the relaxation rate determination. The images taken initially and during the relaxation were analyzed using commercially available software to determine the volume of the drop and the variation of the dimensions of the elongated drop during the relaxation. We measured two representative dimensions of the elongated drop, the length, L , and the width at the middle, W , as a function of the elapsed time. These parameters were related to the viscosity by a relaxation model of Mo, Zhou & Yu [1] that has been successfully used for the determination of the interfacial tension between two immiscible polymer melts. The model relates the shape evolution during relaxation to the physical properties of the working fluids. In their three-dimensional model, the drop shape is described by a symmetric, positive-definite, second-rank tensor $\mathbf{S}$ whose eigenvalues represent the square semi-axis of the ellipsoid. With some manipulation of the eigenvalues of $\mathbf{S}$, following relationship was obtained [2]:

$$\eta = -\frac{20\sigma}{19R_0} \left\{ \frac{d}{dt} \left[\ln \left(\frac{L^2 - W^2}{(L^2 - W^2)_0} \right) \right] \right\}^{-1} \quad (1)$$

with L and W representing the length and the width, respectively, of the elongated drop as shown in Figure 3. The subscript 0 refers to some initial state. All the parameters on the right-hand side of equation (1) are measurable quantities, and the viscosity may be obtained.

An interesting observation is that the data includes the early stages of relaxation when the drop is actually two-lobed. In spite of this deviation from the ellipsoidal shape, the linear fit works unexpectedly well. For comparison, the viscosity of the solutions was also determined by a falling ball technique that was commonly used for highly viscous liquids.

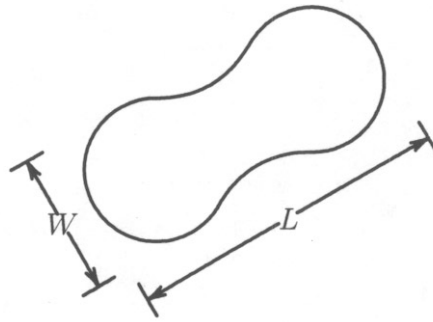


Figure 3. Schematic depicting the measured dimensions in the relaxation experiment.

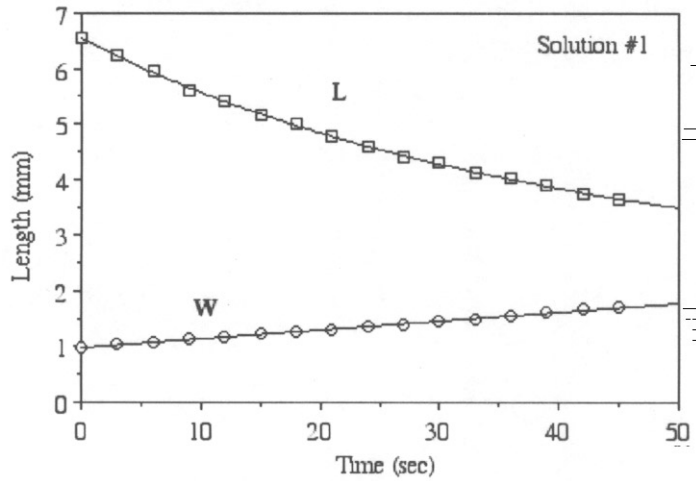


Figure 4. Measured values of L and W as a function of elapsed time.

As mentioned earlier, Figure 2 shows a sequence of the shape relaxation of an elongated drop ($R_0=1.3$ mm, $\eta=1.2 \times 10^3$ Pa s at 28°C). The images are the top view of the drop. The small dark spots in the drop are the air bubbles of varying size. The time interval between two consecutive images is 3 seconds. The elongated drop was not completely stationary but exhibited slow rocking and translational motions, which does not significantly affect the relaxation process.

Experimental results for the sugar-solution test case have been obtained and agree quite well with measurements using the falling ball method. The measured values of $L(t)$ and $W(t)$ show a fairly linear behavior with time as shown in Figure 4. The shape evolution parameter, $\ln \Psi$, is plotted in Figure 5 as a function of time. A linear behavior with a negative slope is seen, and it is quite straightforward to interpret the viscosity. An interesting observation is that the data includes the early stages of relaxation when the drop is actually two-lobed. In spite of this deviation from the ellipsoidal shape, the linear fit works unexpectedly well.

Figure 6 shows the viscosity, η determined by the falling ball technique vs. the viscosity, η_d determined by the present technique in the logarithm scale. As seen in the figure, a correlation exists for Solutions #1 and #2, but not for Solution #3. We suspect that the viscosity values for Solution #3 are strongly affected by the drop rotation that sometimes lasts more than 4 seconds. The current apparatus does not have capability to vary the temperature of the drop, which prevents us performing the measurement on actually undercooled liquids. Even if the apparatus is capable of varying the temperature, we can only perform the measurements on low density liquids ($< 2 \text{ g/cm}^3$) on Earth due to a limited capability of the acoustic levitation. An advantage of the present technique is its capability of determining the surface tension of the drop from the measurement of the angular velocity at the bifurcation because the normalized angular velocity has a unique value at the bifurcation point. One of the shortcomings of the present technique is that it can only be used for highly viscous liquids ($\eta > 10^2 \text{ Pa s}$) because the rotation of the elongated drop cannot be stopped instantaneously. On the other hand, the resonant oscillation technique can only be used for low viscous liquids ($\eta < 10^{-1} \text{ Pa s}$). Therefore, liquids whose viscosities are in the range of $10^{-1} \text{ Pa s} < \eta < 10^2 \text{ Pa s}$ cannot be covered by either technique.

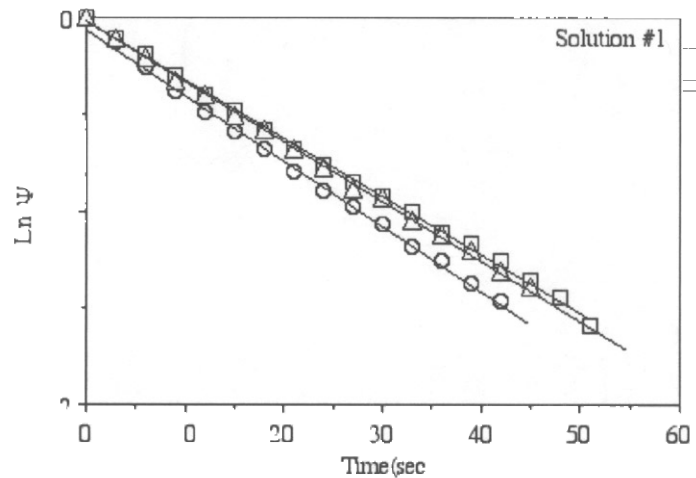


Figure 5. Evolution of the shape parameter Ψ ($\eta = 1.2 \times 10^3 \text{ Pa s}$).

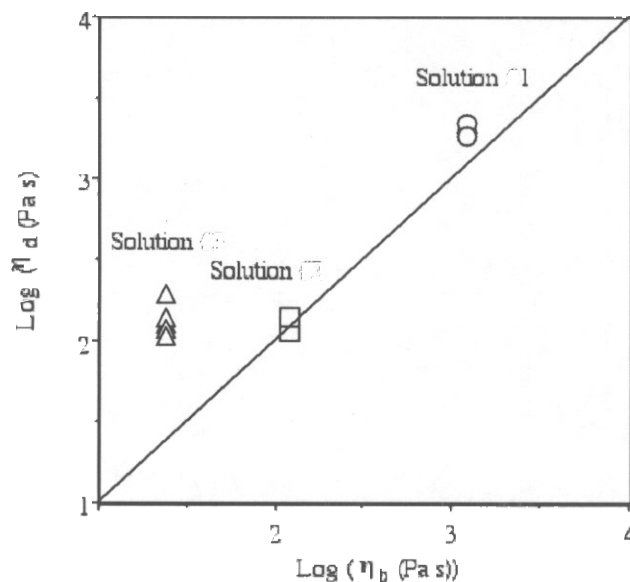


Figure 6. Correlation between η_b , determined by the falling ball technique, vs. η_d , determined by the present technique in the logarithm scale.

2. Thermal Diffusivity Coefficient Measurement

We have also developed a technique that can be used to determine the thermal diffusivity coefficient of undercooled liquids that exist at temperatures below their freezing points. The technique involves levitation of a small amount of liquid in a flattened drop shape using an acoustic levitator and heating it with a laser beam. The heated drop is then allowed to cool naturally by heat loss from the surface. Due to acoustic streaming, the heat loss mainly occurs through the equator section of the drop. The measured cooling rate in combination with a radial heat conduction model allows us to determine the thermal diffusivity coefficient of the drop.

Figure 7 schematically shows the present experimental settings. An ultrasonic transducer oscillates at approximately 23 kHz and generates a standing wave between the transducer head and the reflector. The reflector is made from a special glass that is transparent to infrared lights. A small object (either a solid or liquid sample) can be levitated near a pressure node of the standing wave. Two video cameras located at the top and side of the levitator capture the images of the levitated object. The captured images may be used to determine the actual dimensions of the object. A CO₂ laser that produces a narrow beam is used to locally heat the object at a small area of fringe. However, when the object is heated locally, it usually starts rotating along the polar axis due to a torque created by the local heating. As a result, the laser beam heats the object equally at every fringe. The absorbed heat flows inward by conduction or convection and raises the object temperature as a whole. Once the object reaches a certain temperature, the laser is turned off and the object is allowed to cool naturally. An infrared (IR) camera (Model: AGEMA THERMOVISION 870) looking down the object captures multicolor images that reflect the temperature distribution on the top surface of the object. The IR images that captured the transient temperature distribution during the cooling process are used to determine the cooling rate of the object. The measured cooling rate in combination with a heat transfer model allows us to determine the thermal diffusivity coefficient of the object.

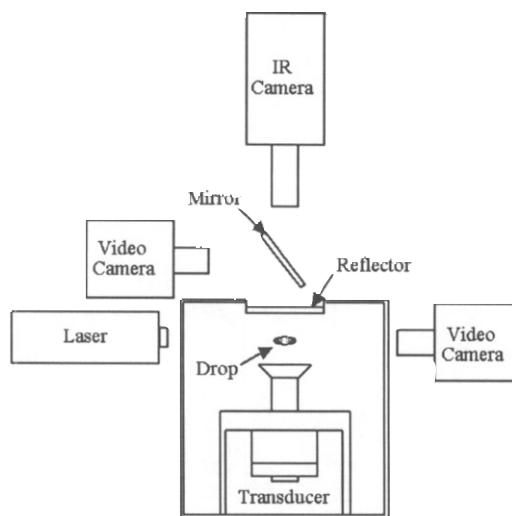


Figure 7. Schematic diagram of experimental apparatus showing the key parts.

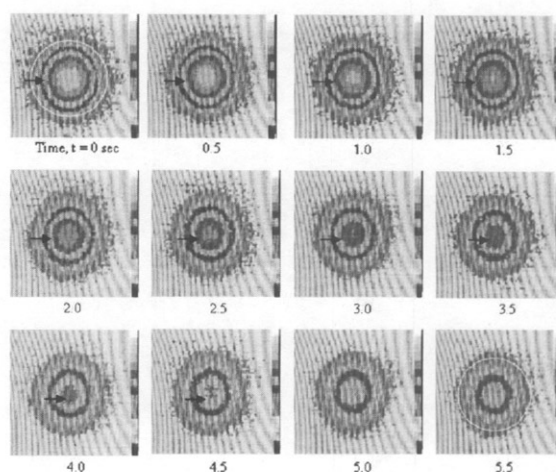


Figure 8. IR images of the top surface temperature of an acoustically levitated glycerin drop as a function of the elapsed time during cooling.

Glycerin was chosen as a model for undercooled liquids. A small amount of glycerin (approximately 15 μl) was introduced into the levitation field with a hypodermic syringe. It was rapidly detached from the syringe and formed into an oblate drop due to the force balance among gravity, surface tension and acoustic pressure. Minimum aspect ratio, a/b of the steadily levitated drop is approximately 1.3, where a and b are the equatorial and polar radii of the drop, respectively. The drop was further flattened to $a/b = 2.6$ by increasing the acoustic pressure. Figure 8 shows a sequence of the IR images of the top surface during the cooling process. The unit of the scale is approximately 5 K. The time interval between two consecutive images is 0.5 seconds. Note that time $t = 0$ sec is set arbitrarily and does not necessarily mean the onset of the cooling process. The white circles superimposed on the first and last images indicate the circumference of the disk. The co-centric rings representing different temperature steps indicate that the surface temperature is not isothermal but varies depending on the distance from the center. The center is the hottest point. As seen in the figure, the rings are slightly distorted in appearance. This distortion

is not real but developed during image processing in the IR camera system, thus it is disregarded. The images reveal the following features of the cooling process. First, elevated temperatures exist outside of the circumference of the disk. This is because the IR camera sees the surrounding air that is heated above room temperature. Secondly, the co-centric rings gradually recede and eventually disappear at the center as the disk cools. Thirdly, although the interior of the drop continuously cools, the temperature at the circumference approximately remains constant at just above room temperature. These features suggest that the heat loss from the acoustically levitated disk is not uniform on every part of the disk surface and mainly occurs at the circumference. The rapidly receding rings are the result of internal heat flow toward the circumference.

The enhanced heat loss at the circumference of acoustically levitated samples can be understood as an act of acoustic streaming. It is known that when an object is placed in an acoustic standing wave, a local streaming is generated around the object [4]. This streaming is distinguished from the global streaming that exists even when the object is not present. We formulated a simple heat conduction model. The heat loss at the top and bottom surfaces was assumed to be minor. We also assumed that the heat loss at the circumference was so strong that its temperature remained constant at near ambient temperature. Under these assumptions, thermal conduction from interior to the circumference controls the heat loss rate and therefore the radial heat conduction model could be justified. We performed the calculation using the known thermal diffusivity coefficient of glycerin and compared the results with the experimental results. The results are shown in Figure 9 in which the coordinates of a specific receding ring is plotted as a function of the elapsed time in

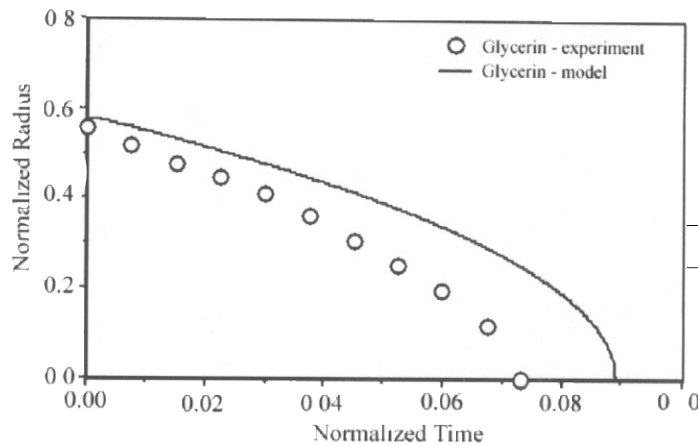


Figure 9. The coordinates of a specific receding ring of the glycerin drop plotted as a function of the elapsed time in the normalized dimensions.

the normalized dimensions. The property parameters used are $a = 2.6 \text{ mm}$ and $\alpha = 0.1 \text{ mm}^2/\text{s}$. As seen in the figure, the model takes roughly 25% longer to disappear. The result can be interpreted in the following way. If the thermal diffusivity coefficient of the materials were not known and the present heat transfer model were used to determine it by matching the calculated receding velocity to the experimental value, the obtained values for glycerin would be larger than the true values by approximately 25%.

The agreement between the experiment and the model turns out to be fair at best because of the simplified heat conduction model. Unconditional applications of the present model to the convective heat loss of acoustically levitated samples may produce inconsistent results. It is obvious that the present assumptions are not met for every acoustically levitated drop. The thermal diffusivity coefficients of glycerin are relatively small comparing some other materials, therefore, internal heat conduction may control the heat

loss rate when the convective heat transfer at the surface is large. This situation is unlikely to occur for high thermal conductive liquids such as metallic drops in which the heat transfer at the surface usually controls the heat loss rate. Even in low thermal conductivity drops, if the heat loss at the top and bottom surfaces becomes significant due to the combination of the drop shape and the acoustic pressure, the model would not work.

Another shortcoming of the present technique is its incapability of setting the acoustic pressure and the aspect ratio of the drop independently. A certain level of the acoustic pressure is needed for levitation in the Earth-based experiments, and an additional pressure is required for flattening the drop. For a given acoustic pressure, the aspect ratio of the drop varies depending on the surface tension of the drop. In other words, we cannot perform the measurement on two different liquids under the exactly same acoustic pressure and the aspect ratio of the drops. This fact prevents us from applying the error analysis performed on the first liquid to the second liquid. For example, the 25% discrepancy found for glycerin drops in the present measurement cannot be applied to water drops.

Despite of the above drawbacks, the present technique is still useful for an intended application to liquids in the undercooled state because the following measuring scheme largely eliminates the shortcomings involved in the technique. First, we levitate a liquid drop at above its freezing point. We apply an additional pressure and fix the acoustic pressure and the aspect ratio. Then, we determine the thermal diffusivity coefficient using the present technique. Since the thermal diffusivity coefficient of the liquid in the normal state is presumably known or can be measured with conventional techniques, we can use it as a reference to calibrate the value determined by the present technique. We next bring the drop in the undercooled state by lowering the temperature but keeping the acoustic pressure and the aspect ratio at the fixed values. Then, we repeat the measurement and apply the same calibration to the measured values. Unfortunately, the current apparatus does not have capability to vary the temperature of the drop, which prevents us to perform the measurement on actually undercooled liquids. More sophisticated heat transfer models that can quantitatively determine the intensity of acoustic streaming around the drop and incorporate it into heat conduction inside of the drop are required for the present technique to be generally applicable to every liquid.

3. Thermocapillary Flow Measurement

Thermocapillary flow measurements of drastically flattened drops have been initiated in the current task. The drastically flattened drop has flows that are dominated by thermocapillary forces because the buoyancy-driven flows are mitigated owing to the low hydrostatic head over the drop thickness. As a result, there is minimal interference from the natural convection, and with thermocapillary flow being isolated, some thermal properties can be inferred from the measurements. For demonstration, a glycerin drop is acoustically levitated and flattened using an acoustic apparatus schematically shown in Figure 7. The drop is then locally heated by a CO₂ laser at the equator. Figure 10(a) shows a steady state thermal image of the top surface of the drop taken by an IR camera. The white circle indicates the physical position of the drop. The laser beam hits at the bottom corner. Heat conduction and convection inside of the drop and strong convective heat loss at the edge of the drop due to acoustic streaming create the temperature distribution that looks like an exclamation mark. Thermocapillary flow associated with this temperature distribution is visualized using tracer particles in Figure 10(b), where the flows start from the bottom corner toward the center and turn to the right or left. The stagnant point exists at the top corner of the drop. We have been developing a model that can describe the above observation.

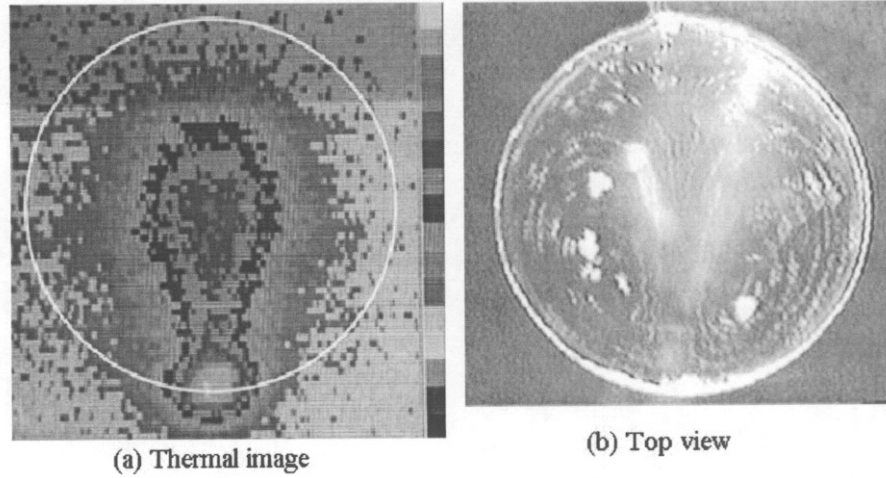


Figure 10. The thermal image and the associated thermocapillary flow of the acoustically levitated and flattened glycerin drop: (a) Thermal image; (b) Thermocapillary flow.

4. Steady Streaming about Levitated Particles

To fully understand the behavior of levitated drops, it has become necessary to treat the detailed fluid dynamics of such systems. Spherical drops were analyzed in detail by Zhao, Sadhal & Trinh [6] for levitation about the node and the antinode. In a forthcoming publication [5], the analysis has been extended for a spherical drop arbitrarily positioned between the node and the antinode.

Oblate Spheroid in a Standing Wave

As a part of the currently supported research, new work has been conducted on the streaming about an oblate spheroid. The results apply to a deformed drop positioned at the velocity antinode. For a horizontally flattened drop placed at the velocity antinode of a standing wave, steady streaming flows are calculated [3]. It is interesting to note that the shear-wave layer (or the Stokes layer) has variable thickness. For small streaming Reynolds number ($Re_s \ll 1$), outer streaming is described by Stokes flow while for $Re_s \gg 1$, there is a boundary-layer structure over the surface of the spheroid. While the results are valid for all aspect ratios, the physical limitation of the actual shape of the flattened drop being approximated as a spheroid still applies. For aspect ratios up to two, the oblate spheroid is a very good approximation to the physical situation. However, for the drastically flattened drop, more work is needed.

We have studied the steady streaming appearing when an oblate spheroid performs small-amplitude high-frequency translational oscillations parallel to its symmetry axis and relative to an incompressible host fluid. This approximates a spheroid placed at the velocity antinode of a standing wave with a large wavelength relative to the particle size. With velocity amplitude U_∞ , and frequency ω , and l to be a length scale, we choose typical dimensionless parameters,

$$\varepsilon = \frac{U_\infty}{\omega l}, M^2 = \frac{\omega l^2}{\nu} \quad (2)$$

with the asymptotic limits for high frequency,

$$\text{with } \varepsilon \ll 1, M \gg 1 \quad (3)$$

We use the oblate spheroidal coordinate system to conform to the shape of the spheroid. The flow field is represented as a superposition of unsteady and steady parts, separately in the (asymptotically thin) Stokes layer at the body surface and the main bulk of the fluid outside the Stokes layer. The solutions in the two regions are connected by the matching requirement. Our analysis has focused on obtaining the leading-order result for the steady part, which just represents the steady streaming. In view of the symmetry of the problem, all steady distributions and fields are symmetric with respect to the equatorial plane of the spheroid.

The inner streaming (in the Stokes layer) is illustrated in Figure 11. The flow does not fade away at the outer edge of the Stokes layer and results in what is seen on the scale of the main bulk of the fluid as the effective slip velocity at the body surface. The latter is given in Figure 12, and serves as a boundary condition for the outer streaming. The slip velocity is always directed from the equator of the oblate spheroid towards its poles.

The outer streaming (in the main bulk of the fluid) is governed by the steady Navier-Stokes equation, with the streaming Reynolds number defined as

$$R_s = \varepsilon^2 M^2 = \frac{U_\infty^2}{\omega \nu} \quad (4)$$

The boundary conditions consist of zero normal velocity and the effective slip velocity which is the only driving factor. The fact that it is the ordinary (without additional terms) Navier-Stokes equation, as well as that the Eulerian mean flow is not different from the Lagrangian one and does not depend on whether the particle or the fluid medium is at rest in the laboratory frame of reference, are all together consequences of the leading-order oscillatory flow being in a single phase in the outer region.

In the limit of a small streaming Reynolds number, the Stokes (creeping flow) solution for the outer streaming is described by the flow patterns are shown in Figure 13. At a large streaming Reynolds number, the outer streaming has a boundary-layer structure over the body surface, the boundary layer being always much thicker than the Stokes layer. The solution has been obtained numerically, and some results are shown in Figures 14, 15 and 16. The boundary-layer flow has been found to proceed smoothly, for all aspect ratios of the oblate spheroid, from the equator to the poles, where it meets a geometric singularity. Upon its self-collision at the poles, the flow is expected to turn around to form circular jets emanating from the body along the symmetry axis. Outside the boundary layer and the jets, the steady flow is potential and of asymptotically lower intensity. It is fully determined by the entrainment into the boundary layer as the one into the jets is negligibly small. The result are illustrated in Figure 17. Topologically, the steady streaming around an oblate spheroid always looks similar to that for a sphere. However, as a matter of further quantitative and qualitative details, two tendencies become apparent as the aspect ratio is decreased (while the amplitude of oscillations and the major radius remain constant). First, the streaming intensity grows appreciably. Second, the zone of most intense streaming shrinks and localizes in a smaller and smaller vicinity of the equator.

The above two tendencies are further underscored by our analysis in the limit of a small aspect ratio (the disk limit; however the amplitude of oscillations and the thickness of the Stokes layer are still assumed much smaller than any linear size of the body). The scaling of the velocity and the coordinate along the surface in fact show this clearly in the near-equator zone of most intense streaming (zone I).

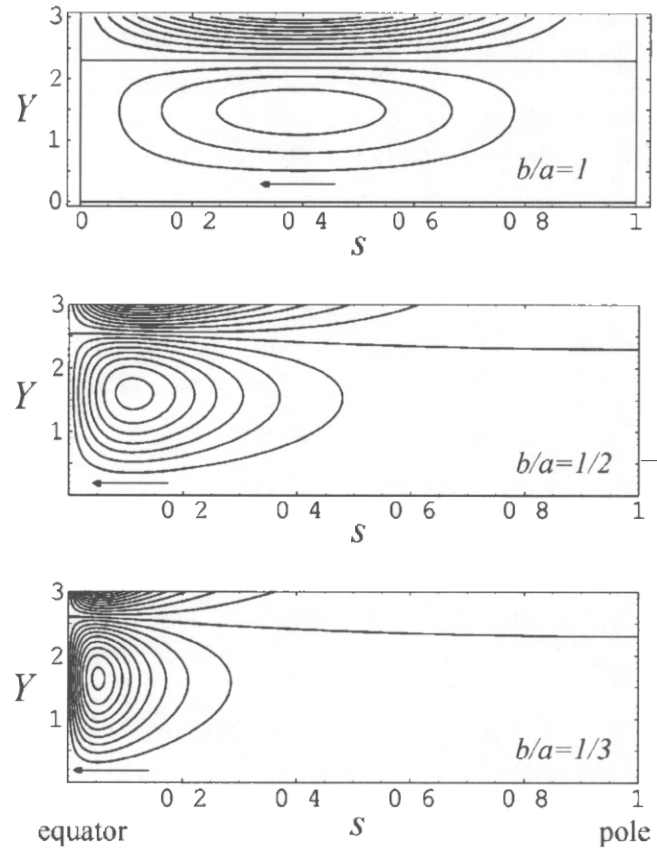


Figure 11. Steady streaming pattern in the Stokes layer at the surface of an oblate spheroid, equation for various aspect ratios. The flow is shown in the domain formed by the normalized distance along the surface (horizontal) and the scaled distance from the surface (vertical). Here $s=0$ corresponds to the equator and $s=1$ to the pole of the spheroid. The vertical scale is highly exaggerated for clarity. The arrows indicate direction of the flow. The streamlines are drawn at the intervals 0.03, 0.1 and 0.3 for the three cases shown, respectively.

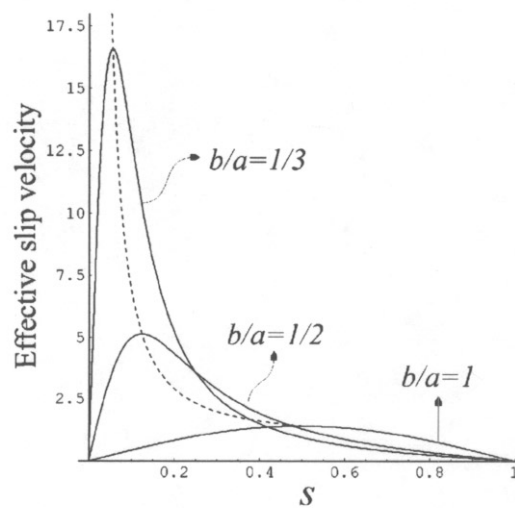


Figure 12. The effective slip velocity persisting at the outer edge of the Stokes layer as a function of the normalized distance along the surface for various aspect ratios ($b/a = 1/3$; $1/2$ and 1). It is directed from the equator ($s=0$) towards the pole ($s=1$).

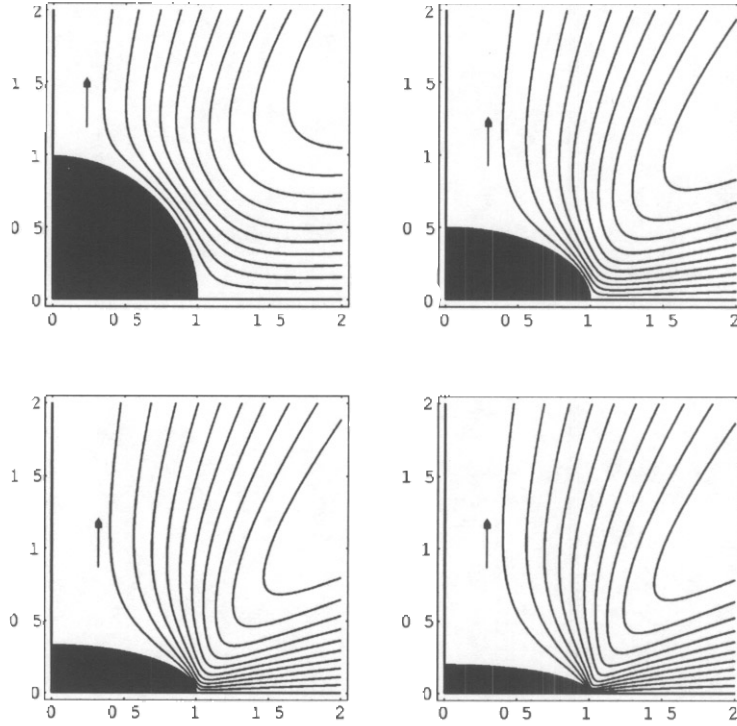


Figure 13. The outer streaming in the Stokes approximation for aspect ratios: $b/a = 1$ (a sphere), $1/2$, $1/3$, and $1/5$. In view of the symmetry with respect to both the axis (vertical) and the equatorial plane (horizontal), only one quadrant of the flow pattern is displayed. The arrows indicate direction of the flow. The streamlines are drawn at the intervals 0.0416, 0.0816, 0.150 and 0.400 for the above four cases, respectively.

There we note that the coordinate scaling characterizes both the distance from the equator and the size of the zone. The geometric size of zone *I* proves to be of the order of the radius of curvature at the equator of the oblate spheroid. Despite the asymptotically shrinking size, the velocity grows so fast that the streaming Reynolds number defined locally for zone *I* actually increases with decreasing the aspect ratio. Outside this small zone, in what we refer to as zone *II* or the main zone, the streaming intensity has an asymptotically lower value. The intensity reduction is much more drastic for the inner streaming, and as a consequence the effective slip velocity, than for the outer streaming. Thus, the outer streaming in zone *II* is determined by its natural decay away from zone *I* while the effective slip velocity at the body surface is negligible.

The concept of the two zones proves well tractable within the boundary-layer approach corresponding to a large streaming Reynolds number. In zone *II*, the boundary-layer flow is over a circular disk with no slip at the surface and is excited by a wall jet which blows from along the disk circumference inwards. The wall jet represents the net action of flow acceleration in zone *I* as it is seen from the standpoint of zone *II*. The integral fluid entrainment into the boundary layer is asymptotically smaller for zone *I* than for zone *II*. Therefore, the potential flow outside the boundary layer is determined by the entrainment into zone *II*.

From the viewpoint of the steady streaming, the disk limit is not universal, but rather shape-dependent. We have studied it quantitatively for the family of oblate spheroids. The results would be different for other shapes. However, qualitatively, what we have established is expected to hold for other disk-like axisymmetric bodies with smoothly rounded edges. In particular, this concerns the scalings. As we have

pointed out, the smallness parameter which puts the oblate spheroid in asymptotic correspondence with another disk-like body in the disk limit is actually not the aspect ratio, but rather the ratio of the radius of curvature in the vicinity of the edge to the major radius, i.e., the dimensionless radius of curvature.

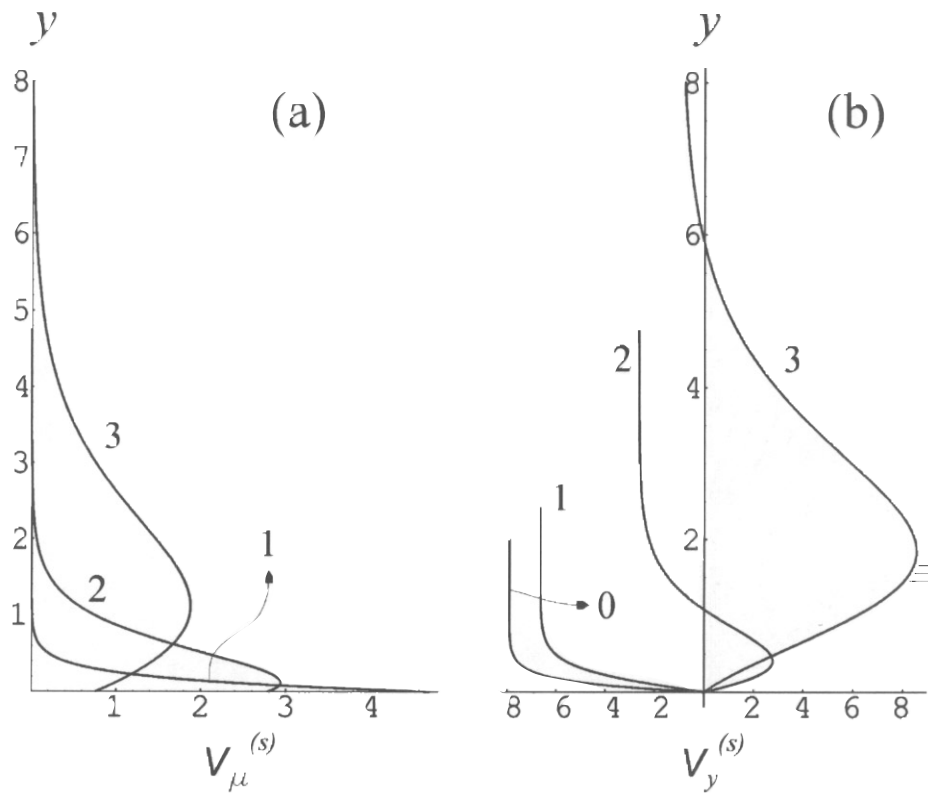


Figure 14. Boundary-layer profiles of (a) the tangential velocity and (b) the normal velocity *versus* the normal coordinate. The results shown are for the spheroid with aspect ratio $b/a = 1/2$. The numbering of the curves corresponds to the following locations along the surface: “0” for $\mu = 0$ ($s = 0$, the equator), “1” for $\mu = 0.2$ ($s = 0.0848$), “2” for $\mu = 0.6$ ($s = 0.310$), and “3” for $\mu = 0.9$ ($s = 0.637$).

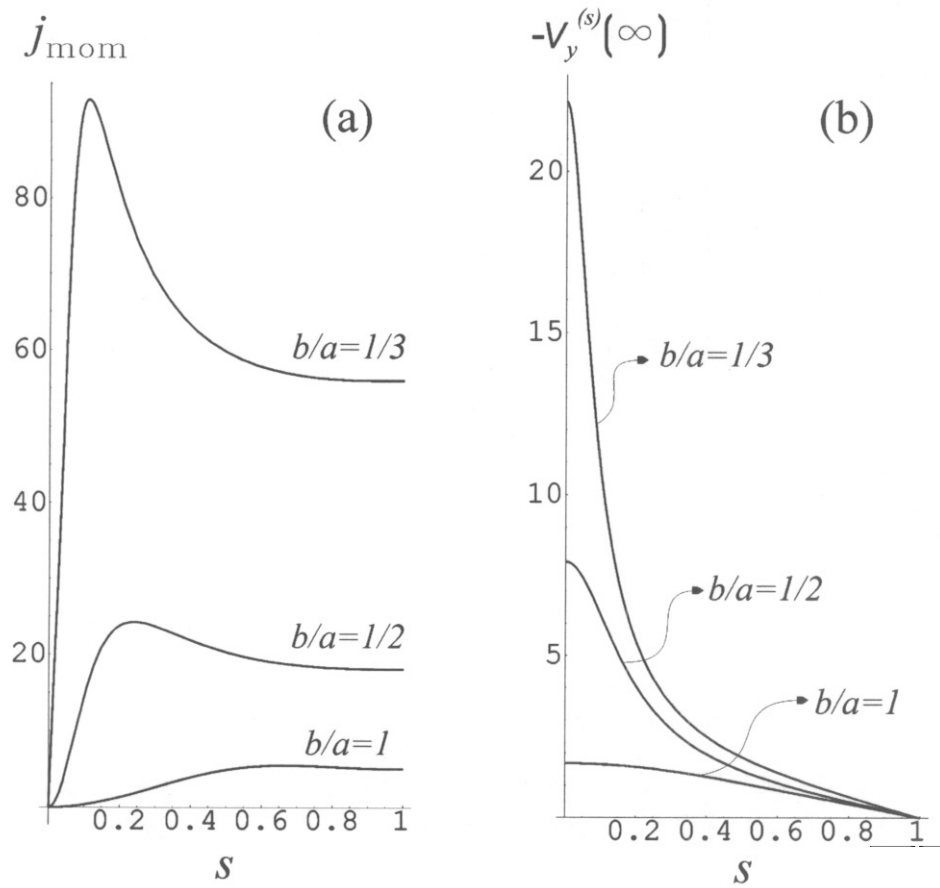


Figure 15. Distributions of (a) the momentum flux and (b) the entrainment velocity along the boundary layer for various aspect ratios.

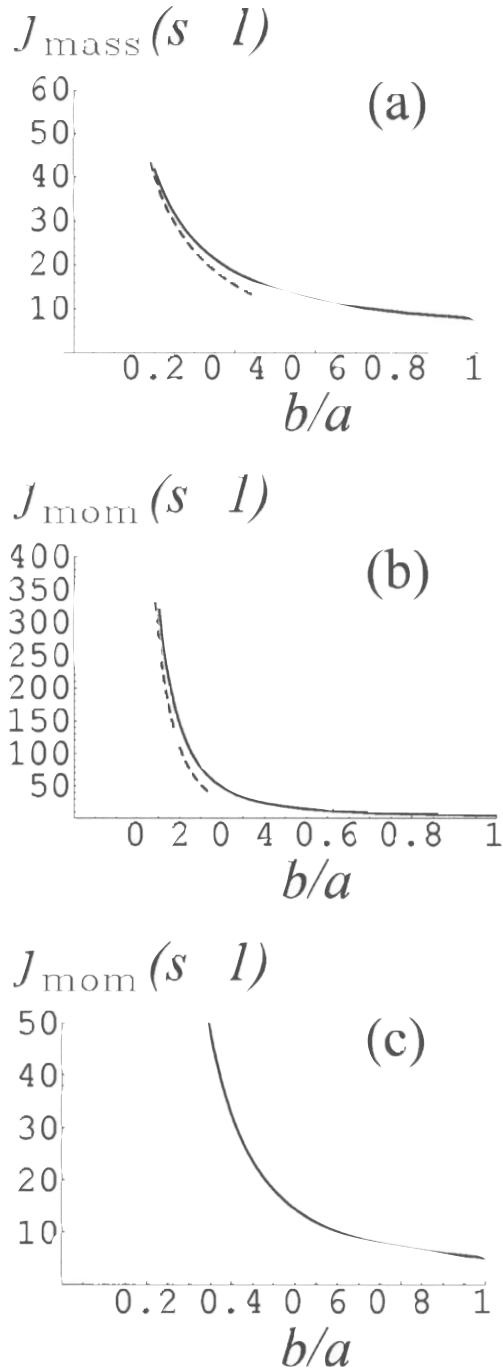


Figure 16. The (a) mass and (b) momentum fluxes in the boundary layer at the self-collision point at the pole taken at $\mu = 1$, as a function of the aspect ratio. Shown in (c) is an enlarged view of (b) for relatively low values of $j_{\text{mom}}(1)$. The dashed curves correspond to the asymptotic consideration in the disk limit.

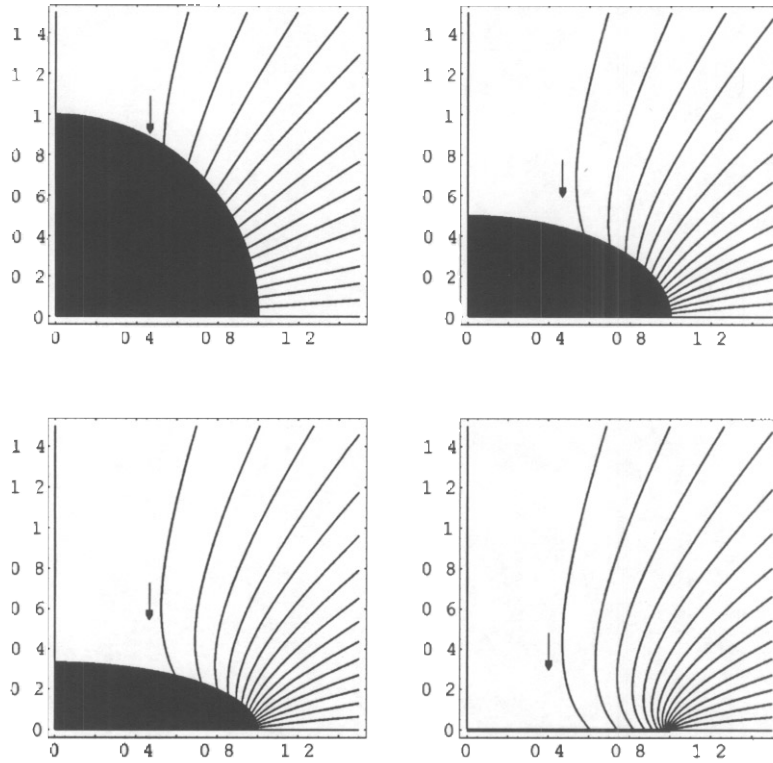


Figure 17. The streaming flow in the main bulk of the fluid at large Reynolds number, determined by the entrainment into the surface boundary layer, for various aspect ratios: $b/a = 1, \frac{1}{2}, \frac{1}{3}$, and 0 (disk asymptotics). The arrows indicate direction of the flow. The streamlines are drawn at the intervals $0.0785R_s^{-1/2}, 0.145R_s^{-1/2}, 0.225R_s^{-1/2}$ and $0.0457A\lambda_0^{-3}\bar{R}_s^{-1/2}$ for the above four cases, respectively.

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FROM OXYGEN GENERATION TO METALS PRODUCTION: *IN SITU* RESOURCE UTILIZATION BY MOLTEN OXIDE ELECTROLYSIS

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For the exploration of other bodies in the solar system, electrochemical processing is arguably the most versatile technology for conversion of local resources into usable commodities: by electrolysis one can, in principle, produce (1) breathable oxygen, (2) silicon for the fabrication of solar cells, (3) various reactive metals for use as electrodes in advanced storage batteries, and (4) structural metals such as steel and aluminum. Even so, to date there has been no sustained effort to develop such processes, in part due to the inadequacy of the database. The objective here is to identify chemistries capable of sustaining molten oxide electrolysis in the cited applications and to examine the behavior of laboratory-scale cells designed to generate oxygen and to produce metal.

The basic research includes the study of the underlying high-temperature physical chemistry of oxide melts representative of lunar regolith and of Martian soil. To move beyond empirical approaches to process development, the thermodynamic and transport properties of oxide melts are being studied to help set the limits of composition and temperature for the processing trials conducted in laboratory-scale electrolysis cells. The goal of this investigation is to deliver a working prototype cell that can use lunar regolith and Martian soil to produce breathable oxygen along with metal by-product. Additionally, the process can be generalized to permit adaptation to accommodate different feedstock chemistries, such as those that will be encountered on other bodies in the solar system.

The expected results of this research include (1) the identification of appropriate electrolyte chemistries; (2) the selection of candidate anode and cathode materials compatible with electrolytes named above; and (3) performance data from a laboratory-scale cell producing oxygen and metal. On the strength of these results it should be possible to assess the technical viability of molten oxide electrolysis for *in situ* resource utilization on the Moon and Mars. In parallel, there may be commercial applications here on earth, such as new “green” technologies for metals extraction and for treatment of hazardous waste, e.g., fixing heavy metals.

Introduction

There is plenty of oxygen on the Moon to sustain life — indeed, the lunar surface is over 60% oxygen¹. Martian soil is about 45% oxygen². However, all of this is chemically bound to other elements in the form of very stable compounds. Molten oxide electrolysis is a candidate technology for exploiting local resources in order to produce breathable oxygen along with a host of valuable by-products such as silicon for use in solar cells, reactive metals for use in advanced storage batteries, and steel and aluminum for use in construction³. No special reagents need to be transported from earth in order to employ the technology. The only process input that needs to be furnished on site is electric power and this, presumably, can be generated either photovoltaically or by nuclear fission. Furthermore, it has been shown that molten

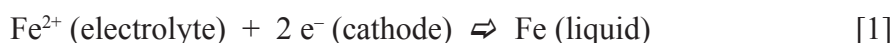
Keywords: oxygen generation, metal production, *in situ* resource utilization (ISRU), electrolysis

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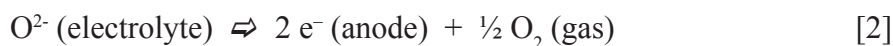
oxide electrolysis has potential for treating certain forms of hazardous waste produced by the metals and chemicals industries⁴. This shows that the process has the flexibility to be adaptable to different feedstocks, an attribute making it attractive for use with the resources available on the Moon or Mars.

Molten oxide electrolysis is an extreme form of molten salt electrolysis, a technology that has been producing tonnage metal for over 100 years; aluminum, magnesium, lithium, sodium, and the rare-earth metals are all produced in this manner. What sets molten oxide electrolysis apart is its ability to produce oxygen gas at the anode. No contemporary electrolytic technology can do this. Indeed, in the light of the push to reduce greenhouse gas emissions in the metals industry one of the greatest challenges for the aluminum industry is the replacement of the consumable carbon anode (which produces CO₂) with a nonconsumable anode which would produce oxygen⁵. So molten oxide electrolysis then both avoids the use of molten halide electrolytes and enables the production of oxygen gas.

Figure 1 shows how iron and oxygen might be produced by the proposed technology⁴. The electrolyte in this case is a multicomponent solution consisting of iron oxide and other oxides, such as silica, alumina, magnesia, and calcia. All of these oxides are highly abundant in the lunar regolith¹ and Martian soil². The cathode is a pool of molten iron at the bottom of the cell. At the interface of liquid metal and electrolyte, the electrochemical reduction of iron occurs according to the following reaction:



The origin of the Fe²⁺ is the iron oxide feed, which has dissolved in the molten oxide electrolyte and dissociated to form Fe²⁺ cations and O²⁻ anions. The liquid iron produced is instantly incorporated into the metal pool without the need for mass transport to another site within the cell. Thus, as the reaction proceeds, the depth of the iron pool increases. The solid member forming the floor of the cell and also acting as current collector must be made of a material that is chemically inert in contact with molten iron and also is a good electronic conductor. Materials satisfying these requirements include certain electronically conducting oxides and refractory hard metals, as well as thermally graded materials such as “cold fingers” around which iron has frozen. At the top of the cell is the anode, which acts as the current feeder. The anode must be chemically inert with respect to both oxygen gas and the molten oxide electrolyte. Evolution of oxygen occurs according to the following reaction:



The source of O²⁻ is the iron oxide feed which has dissolved and dissociated in the molten oxide electrolyte. The anode functions as an electron sink, and the product oxygen gas evolves as bubbles on the surface of the anode and floats to the surface of the melt. Candidate anode materials include electronically conducting oxide and metals protected by an oxide film on the surface⁶. The sidewall consists of electrolyte frozen against a shell made of refractory brick. This is the electrolytic equivalent of skull melting, and is precisely the condition in a modern Hall cell producing tonnage aluminum. Feed consisting of iron oxide is added to the cell from the top. The process is continuous. Periodically, metal is removed from the cell by siphoning.

What about the engineering aspects of the reactor depicted in Figure 1? At 1800 K, the standard free energy of formation of FeO is -159 kJ/mol⁷ which via the Nernst equation gives a standard decomposition

potential of 0.825 V. Although, strictly speaking, there is no formal relationship between the value of the decomposition potential (a *thermodynamic* quantity) and the value of the steady-state voltage in an industrial cell operating under conditions of controlled current, molten salt electrolysis cells (aluminum, magnesium, etc.) are observed to operate at about 2 to 3 times theoretical voltage in order to surmount *kinetic* barriers associated with the electrode reactions and to keep the electrolyte molten by Joule heating⁸. Accordingly, we can expect the cell in Figure 1 to operate at about 2 to 3 V. The value of the current will be governed by the thermal balance of the cell: the current must exceed a minimum level in order to generate adequate Joule heat to keep the electrolyte molten. Given the thermal and electrical properties of molten salts, it turns out that the threshold of thermal sustainability is 1 kA. In one hour, such a cell would produce 1.04 kg iron and 0.30 kg oxygen or 0.23 standard cubic meters oxygen. Current densities in molten salt cells are in the vicinity of 1 A cm^{-2} . This means that the anode would be on the order of 30 cm in diameter, immersed in the electrolyte to a depth of 1 cm. This translates into a rather compact device with a small footprint. Productivity scales linearly with these dimensions, i.e., to double the production of oxygen one would double the anode area and hence double the current through the cell; voltage remains unchanged. The oxygen produced at the anode bubbles through the electrolyte and rises to the top of the cell for collection. Molten iron needs to be periodically harvested, and this is typically done by siphon. All that is required to keep the oxygen coming is iron oxide (about 1.4 kg h^{-1}) and electric power (2 to 3 kVA).

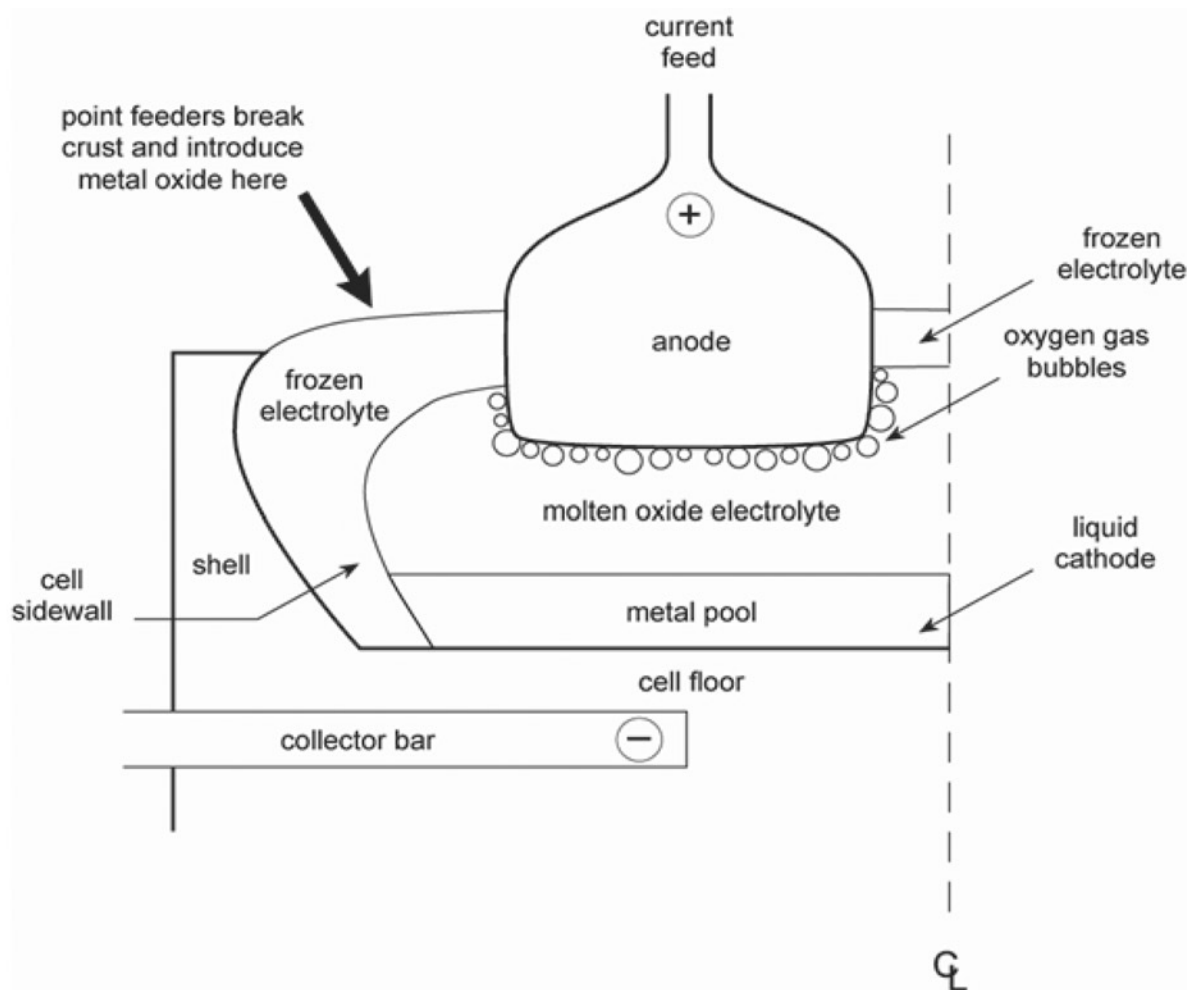


Figure 1. Schematic of cell for the production of oxygen by molten oxide electrolysis.

Accurate knowledge of the electrical properties of molten salts is paramount in the design of industrial electrolytic cells because joule heating of the electrolyte is central to establishing the thermal balance of the reactor. Accordingly, the electrical conductivities and transference numbers were measured for various FeO - CaO - MgO - SiO₂ systems.

Experimental

The experimental conditions have been described elsewhere. Electrical conductivity was measured by the coaxial-cylinders technique which was invented in this laboratory⁹. For sample preparation and other experimental details the reader is directed to the paper by Schiefelbein and Sadoway which reports the electrical conductivity measurements of several melts in the CaO - MgO - SiO₂ system¹⁰. Transference numbers were measured by stepped-potential chronoamperometry following the procedure described in the paper by Fried, Rhoads, and Sadoway¹¹.

Results and discussion

Figure 2 shows the effect of FeO on the electrical conductivity of the solvent melt designated S1, the composition of which is 24.59% CaO, 26.15% MgO, 49.26% SiO₂ on a molar basis. Figure 3 shows a similar variation observed in a binary system (48.53 % CaO and 51.47 % SiO₂). It is clear from the figure the value of electrical conductivity increases as the concentration of FeO increases. Figure 4 shows the isothermal variation of electrical conductivity at 1425°C. Conductivity scales with FeO content on a molar basis. This indicates that FeO donates charge carriers that are highly mobile in comparison to what is already present in the solvent melt. We speculate that these carriers are electronically conductive, as evidenced by Figure 5 which shows the electronic transference number rising in tandem with the molar concentration of FeO.

The isothermal variation in electrical conductivity with composition for a multi-component melt is expected to follow

$$\sigma = \sum_i X_i \mu_i z_i^2 \quad [3]$$

where σ is electrical conductivity, X_i is the mole fraction of component i , μ_i is the mobility of component i , and z_i is the net charge of i . Lumping all coefficients exclusive of X_i and assuming negligible interaction between solutes in a multicomponent melt, one can perform a multivariate regression analysis to get a first order estimate of the effect of any given solute on the conductivity of the solution. Figure 6 shows the result at 1425°C for the set of melts investigated in this study. The effect of FeO is seen in two places. Along with CaO and MgO, FeO donates ionic charge carriers and, unlike the alkaline-earth oxides, FeO also contributes electronically conductive carriers as expressed by the coefficient with a value of 2.326, more than twice that of CaO and MgO. Note that the coefficient associated with SiO₂ has a negative value, -0.192, which is in keeping with the fact that SiO₂ does not contribute charge carriers, but instead reduces their population by forming covalent bonds with them.

The measurements made in this work compare favorably to those reported by Haskin et al.¹² insofar as the isothermal variation of conductivity with composition at 1425°C. However, as a data set the values reported by Haskin et al. are systematically about 40% greater in magnitude than those reported in the present study. This, we believe, may be attributable to their use of the ring technique which suffers from the fact that the current path is a function of the electrical properties of (i) the melt under investigation and (ii) the electrodes (9).

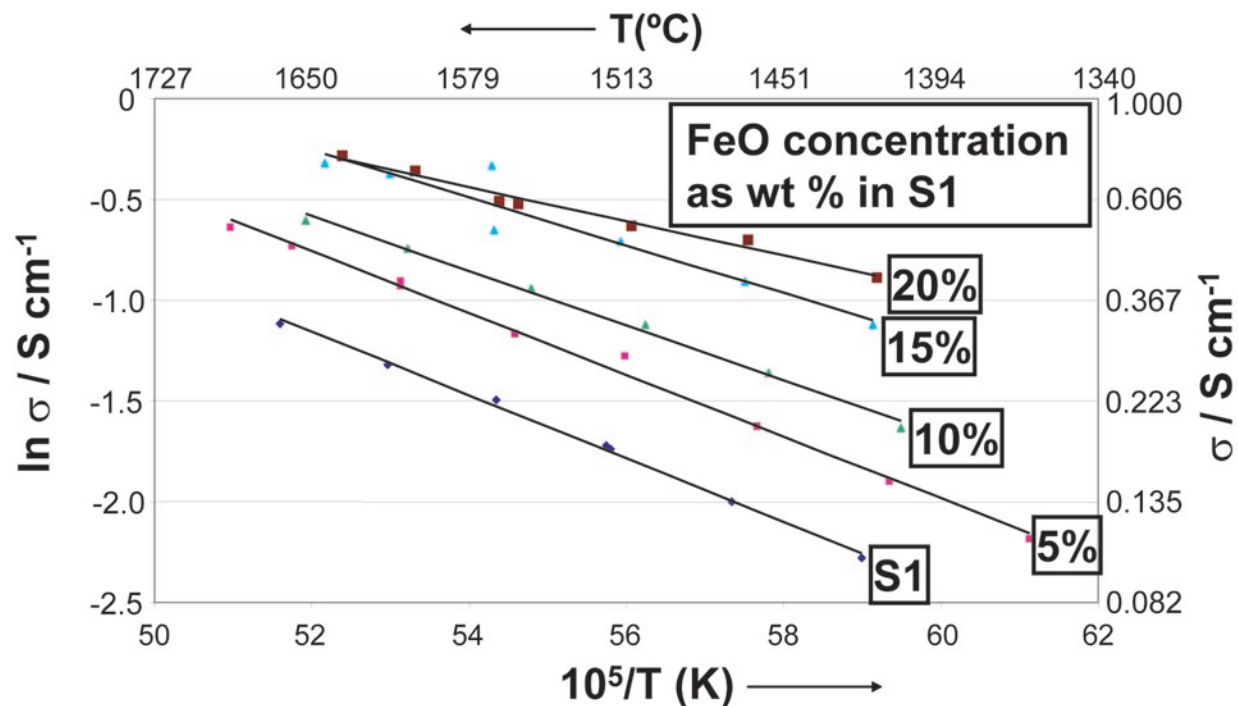


Figure 2. Variation of electrical conductivity with temperature and composition. Composition S1 is 24.59% CaO, 26.15% MgO, 49.26% SiO₂ on a molar basis. The concentration of FeO is given in weight per cent.

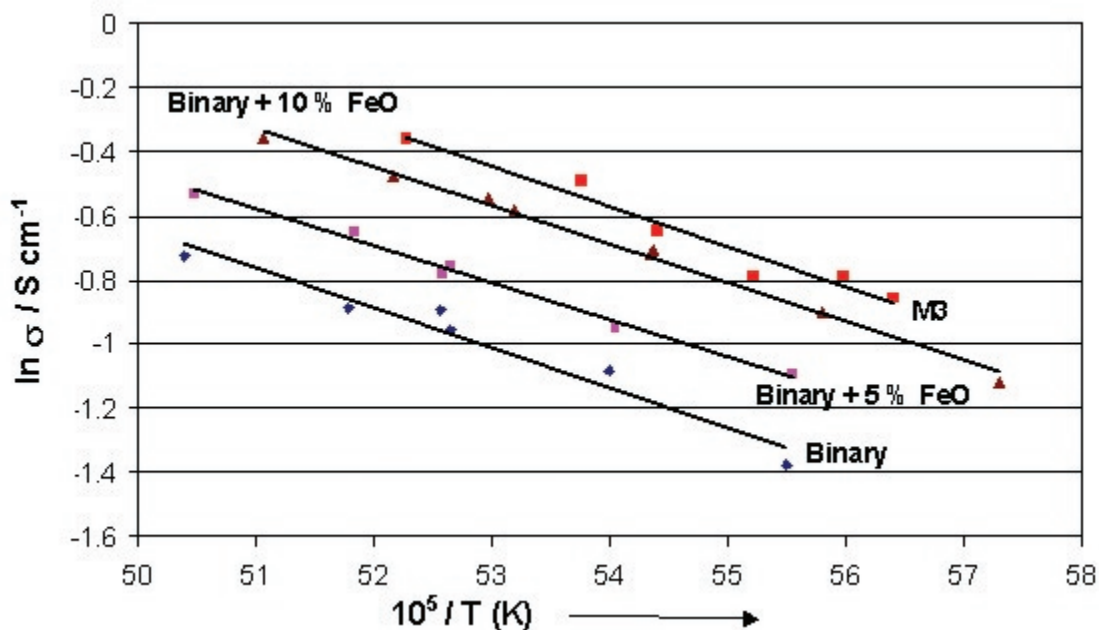


Figure 3. Variation of electrical conductivity with temperature and composition. Composition M3 is 46.03 % CaO, 13.78 % MgO, 40.19 % SiO₂ on a molar basis, binary refers to 48.53 % CaO and 51.47 % SiO₂. The concentration of FeO is given in weight per cent

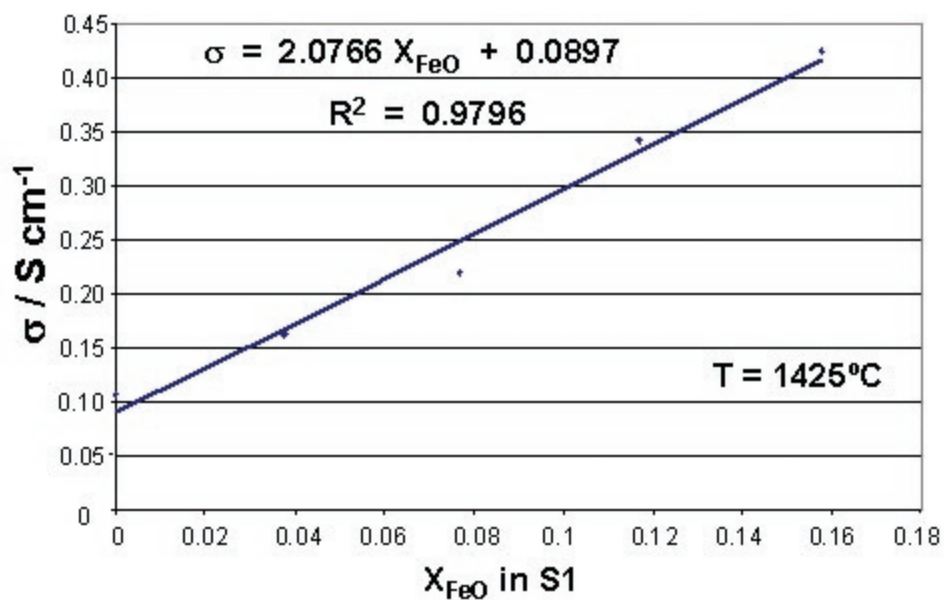


Figure 4. Isothermal variation of electrical conductivity with concentration of FeO.
 $T = 1425^\circ\text{C}$.

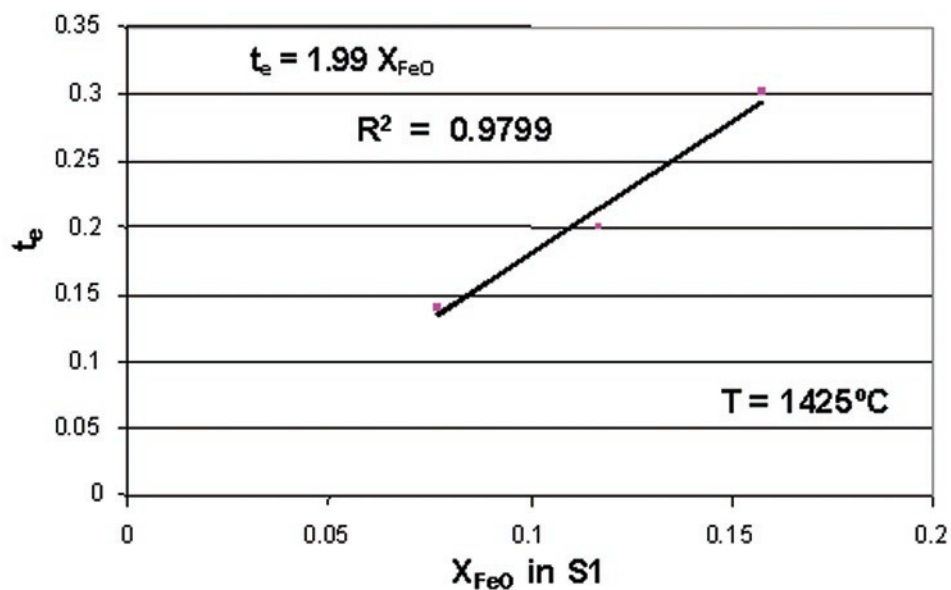


Figure 5. Isothermal variation of electronic transference number, t_e , with concentration of FeO.
 $T = 1425^\circ\text{C}$.

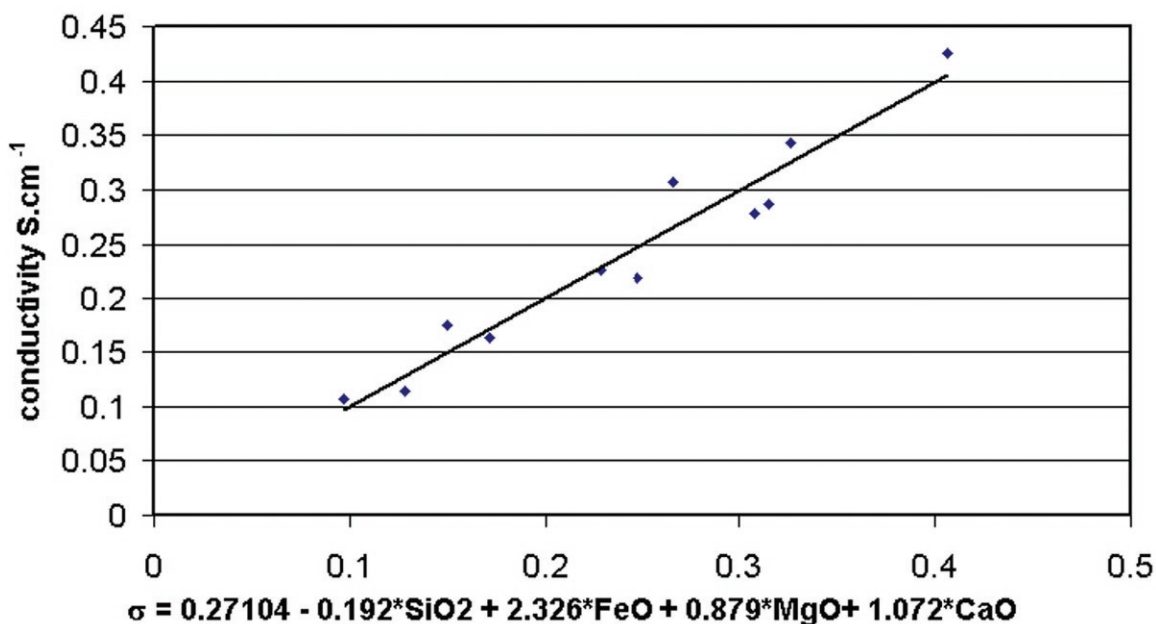


Figure 6. Isothermal variation of electrical conductivity with melt composition at 1425 °C.

Acknowledgments

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LATTICE BOLTZMANN COMPUTATIONS OF BINARY DIFFUSION IN LIQUIDS UNDER STOCHASTIC MICROGRAVITY

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Introduction

We have conducted research to further develop the Lattice Boltzmann (LB) model in liquids as a computational tool to better understand convective diffusion in stochastic microgravity. We focus on the prototype problem of mathematical modeling of binary liquid alloy diffusion couples. Our ultimate objective is to estimate the accuracy of, or make corrections to, binary liquid diffusivities measured in microgravity. The same methodology should be useful to analyze other experiments in microgravity that involve convective diffusion.

It is well known that diffusivities in binary liquids are difficult if not impossible to measure accurately on Earth because of solute transport due to buoyancy driven fluid convection. Consequently, diffusivities have been measured in microgravity, and have resulted in dramatic differences from measurements on Earth¹⁻¹⁰. Nevertheless, there is still some convection in the microgravity environment, and this can affect measured diffusivities. For example, measurements by Smith^{9,10} for alloys of Pb-Au, Pb-Ag, Pb-Sb, Sb-In and In-Sb result in considerable differences of the measured diffusivity D on temperature T : Arrhenius $\ln D \propto 1/T$ on Earth, $D \propto T^2$ in microgravity with g -jitter, and $D \propto T$ in microgravity with a vibrational isolation mount (Canadian Microgravity Isolation Mount, MIM). Values of D are about 50% smaller for measurements using the vibrational isolation mount than with that mount in latched mode. Moreover, for forced vibration of the MIM at 0.3 Hz and amplitude corresponding to $0.004 g_E$, values of D were typically 100% larger than in latched mode. In order to understand these and other measurements, it is necessary to model the influence of residual convection in microgravity on diffusion.

Moreover, even in strictly zero gravity, there are non-solenoidal flows caused by density changes during transient diffusion, and these can be comparable^{11,12} at short times to buoyancy-driven flows in microgravity. This has also been confirmed in numerical computations by Bune et al.¹³ who refer to it as “stealth convection.” Thus, the results of using computational fluid dynamics (CFD) codes based on the Oberbeck-Boussinesq (OB) approximation¹⁴ are unreliable at short times for transient diffusion in microgravity because the OB approximation includes the assumption of solenoidal flows. Since there are also residual accelerations (equivalently residual gravity) in the microgravity environment,¹⁵⁻²² the resulting buoyancy driven flows can affect measured diffusivities.

We decompose the residual acceleration as $\mathbf{g} = \mathbf{g}_s + \mathbf{g}_j$ where $\mathbf{g}_s$ is a rather steady acceleration, due for example to drag, and $\mathbf{g}_j$ is the so-called g -jitter. The component $\mathbf{g}_s$ varies slowly over a time scale that is large compared to the characteristic time scale of g -jitter but small compared to the period of a spacecraft orbit. Such g -jitter can have both deterministic components with some well-defined frequency ω_0 as well as stochastic components that can only be described statistically. A model for g -jitter based on a narrow

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band noise has been proposed and explored in our previous research supported by NASA²³⁻²⁶. It is very difficult to incorporate stochastic accelerations in numerical computations by using CFD. This follows because the use of standard numerical algorithms to solve stochastic differential equations is subject to numerical instabilities and large errors (including apparent convergence to false values), due to the fact that the stochastic terms are not differentiable.²⁷ The LB model²⁸⁻³² is an intrinsically statistical model that can be used to simulate fluid dynamics. For simple problems, it is much less efficient than CFD, but for more complicated problems, such as convective diffusion in binary liquids with stochastic forces, it might well be better.

During the current research period, we have conducted research to determine the effective (apparent) viscosity of Finite Difference Lattice Boltzmann (FDLB) models for a pure fluid, formulated a new split-collision term LB model for a binary fluid, and have begun to investigate boundary conditions for LB models.

I. Viscosity of FDLB Model

The Lattice Boltzmann model is based on a distribution function such that $f(\mathbf{r}, \mathbf{v}, t) d^3x d^3v$ is the number of fluid particles which at time t have positions $\mathbf{r}$ in the volume element d^3x about $\mathbf{r}$ and velocities $\mathbf{v}$ in the volume element d^3v about $\mathbf{v}$. The distribution function is assumed to obey a Boltzmann equation in the relaxation time approximation of the form

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} \right) f(\mathbf{r}, \mathbf{v}, t) = -\frac{1}{\tau} [f(\mathbf{r}, \mathbf{v}, t) - f^{eq}(\mathbf{r}, \mathbf{v}, t)] \quad (1)$$

where $\mathbf{F}$ is the force on a particle of mass m . The distribution relaxes toward its equilibrium value f^{eq} with a relaxation time τ , usually assumed to be a constant comparable to the collision time of fluid particles. The fluid has an average local number density

$$n(\mathbf{r}, t) = \int f(\mathbf{r}, \mathbf{v}, t) d^3v \quad (2)$$

and local velocity

$$\mathbf{u}(\mathbf{r}, t) = \frac{1}{n(\mathbf{r}, t)} \int \mathbf{v} f(\mathbf{r}, \mathbf{v}, t) d^3v \quad (3)$$

In typical LB models, the equilibrium distribution function is taken to be the Maxwell-Boltzmann distribution function

$$f^{eq}(\mathbf{r}, \mathbf{v}, t) = n(\mathbf{r}, t) \left(\frac{m}{2\pi kT} \right)^{3/2} e^{- (m/2kT) [\mathbf{v} - \mathbf{u}(\mathbf{r}, t)]^2} \quad (4)$$

where k is Boltzmann's constant.

For a system not too far from equilibrium, we can approximate the force term in Eq(1) by replacing the distribution function by its equilibrium value. The LB model is then completed by discretizing the velocity space and solving the resulting equations numerically. To discretize, we replace $f(\mathbf{r}, \mathbf{v}, t) d^3v$ for $\mathbf{v} = \mathbf{v}_i$ by $f_i(\mathbf{r}, t)$ and then replace integrals over the velocity by sums over i . Thus the discrete distribution functions obey

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_i \cdot \nabla \right) f_i(\mathbf{r}, t) = -\frac{1}{\tau} [f_i(\mathbf{r}, t) - f_i^{eq}(\mathbf{r}, t)] + \frac{\mathbf{F}}{kT} \cdot [\mathbf{v}_i - \mathbf{u}(\mathbf{r}, t)] f_i^{eq}(\mathbf{r}, t) \quad (5)$$

Eq(5) can be solved numerically by a number of techniques. Some LB models are solved by means of "streaming algorithms" in which the spatial grid is tied to the time steps by means of an equation of the form $\delta \mathbf{r} = \mathbf{v}_i \delta t$. Since $|\mathbf{v}_i| \delta t$ is the order of the mean free path, this limits computations to very small samples. It is far less restrictive, however, to discretize space over distances that are large compared to the mean free

path but small compared to distances over which $n(\mathbf{r}, t)$ and $\mathbf{u}(\mathbf{r}, t)$ vary significantly. This leads to Finite Difference Lattice Boltzmann (FDLB) models, which we use.

We have used Chapman-Enskog expansions and computer simulations to study the effective viscosity of FDLB models.³³ The distribution function and quantities derived from it are expanded to second order in the Knudsen number $\varepsilon = c\tau/L$ where $c \sim (kT/m)^{1/2}$ is the mean thermal speed of a particle, $c\tau$ is the mean free path, and L is a length characteristic of the system size. The physical viscosity of this model, obtained from Eq(5) prior to discretization of space and time, is found to be³³

$$v_0 = \frac{\tau kT}{m} \quad (6)$$

The apparent (effective) viscosity depends on the finite difference scheme used to solve the LB equations *after* discretization of space and time. It is the sum of the physical viscosity and a spurious numerical viscosity. This spurious numerical viscosity is positive for first order upwind Lax and Lax-Wendroff schemes and vanishes for space centered and second order upwind schemes. For the first order upwind scheme we find³³

$$v = v_0 \left[1 + \frac{\delta s}{2c\tau} \right] \quad (7)$$

where δs is the increment of spatial discretization. For conventional LB models for which $\delta s = c\tau$, Eq(7) becomes

$$v = v_0 \left[1 + \frac{\delta t}{2\tau} \right] \quad (8)$$

which holds for the Lax-Wendroff scheme for general δs . For the Lax scheme, we find

$$v = v_0 \left[1 + \frac{(\delta s)^2}{2c^2\tau\delta t} \right] \quad (10)$$

These apparent viscosities have been verified by computer simulation for the decay of shear waves between parallel plates. The results are presented in Figure 1 versus δs and in Figure 2 versus δt .

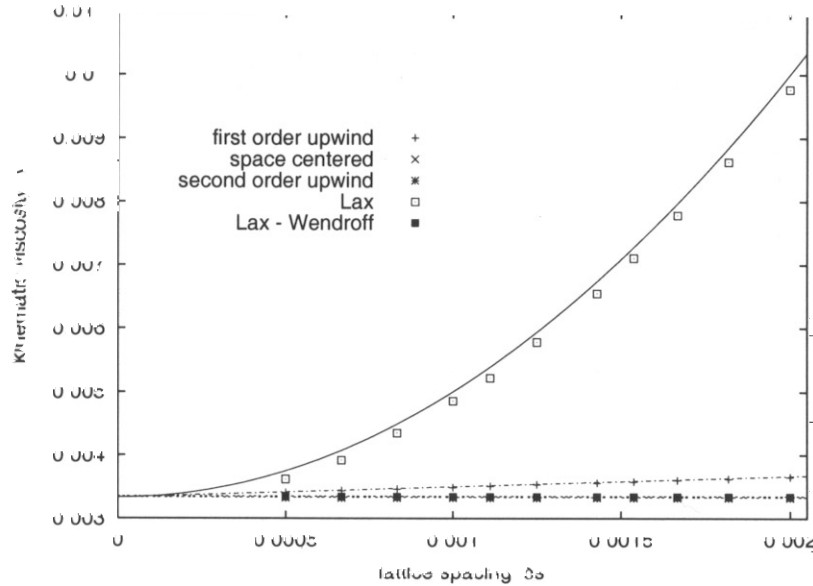


Figure 1. Plot of the apparent kinematic viscosity versus spatial discretization δs for fixed δt for the decay of shear waves in a channel of unit width for $\tau = 0.01$, $\delta t = 0.0001$ and $c = 1$. Note that v is linear for the first order upwind scheme Eq(7) and quadratic for the Lax scheme Eq(10), as expected.

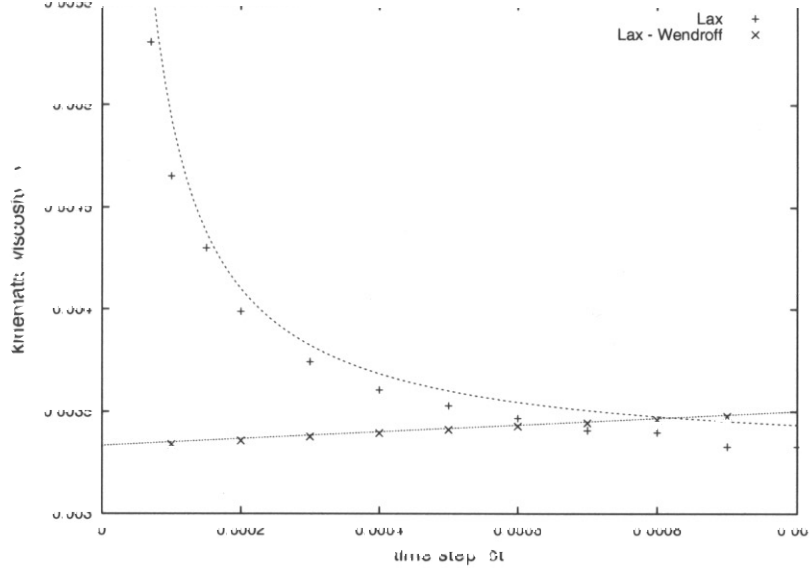


Figure 2. Plot of the apparent kinematic viscosity versus spatial discretization δt for fixed δs for the decay of shear waves in a channel of unit width for $\tau = 0.01$, $\delta s = 0.001$ and $c = 1$. Note that v is linear for the Lax-Wendroff scheme Eq(8) while for the Lax scheme the correction term varies inversely with δt , as expected from Eq(10).

From these computations, we conclude that the apparent viscosity of FDLB models depends on the scheme used to solve them. The spurious numerical viscosities can be eliminated by going to higher order schemes, but these are more computationally intensive.

II. New Model for Binary Systems

LB models for a binary system can be developed by adding a superscript $\sigma = A, B$ to denote the chemical species and replacing Eq(1) by a pair of coupled Boltzmann equations for the distribution function $f^\sigma(\mathbf{r}, \mathbf{v}, t)$ of the form

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} + \frac{\mathbf{F}^\sigma}{m^\sigma} \cdot \nabla_{\mathbf{v}} \right) f^\sigma(\mathbf{r}, \mathbf{v}, t) = -\frac{1}{\tau^\sigma} [f^\sigma(\mathbf{r}, \mathbf{v}, t) - f^{\sigma,eq}(\mathbf{r}, \mathbf{v}, t)] \quad (11)$$

Each species has a local average number density

$$n^\sigma(\mathbf{r}, t) = \int f^\sigma(\mathbf{r}, \mathbf{v}, t) d^3v \quad (12)$$

and local velocity

$$\mathbf{u}^\sigma(\mathbf{r}, t) = \frac{1}{n^\sigma(\mathbf{r}, t)} \int \mathbf{v} f^\sigma(\mathbf{r}, \mathbf{v}, t) d^3v \quad (13)$$

The barycentric velocity of the fluid is

$$\mathbf{u} = \frac{\rho^A \mathbf{u}^A + \rho^B \mathbf{u}^B}{\rho^A + \rho^B} \quad (14)$$

where $\rho^\sigma = m^\sigma n^\sigma$ is the local density of species σ .

We have reformulated the Lattice Boltzmann model for binary fluids by incorporating two relaxation times for each species, one for interaction with like atoms and the other for interaction with unlike atoms.

The collision term on the right hand side of Eq(11) is replaced by a split collision term of the form³⁴

$$\Omega^\sigma = -\frac{1}{\tau_{\sigma\sigma}}[f^\sigma - f^{\sigma,eq}] - \frac{1}{\tau_{\sigma\bar{\sigma}}}[f^\sigma - \tilde{f}^{\sigma,eq}] \quad (15)$$

where σ with and without an overbar designate opposite species. For example, if $\sigma = A$, then Eq(15) contains two relaxation times τ^{AA} and τ^{AB} and two equilibrium distribution functions of the *general* form of Eq(4). We treat an isothermal system. For local equilibrium we must have $\mathbf{u}^A = \mathbf{u}^B = \mathbf{u}$ which leads to the conclusion that the *equilibrium* distribution functions in Eq(15) are the same. Consideration of the fact that momentum must be conserved locally for collisions shows that the relaxation times are related through the local species densities. One ultimately gets a self-consistent equation of the same form as Eq(11) except³⁴

$$\frac{1}{\tau^A} = \frac{1}{\tau^B} = \frac{n^A}{\theta^A} + \frac{n^B}{\theta^B} \equiv \frac{1}{\tau} \quad (16)$$

where θ^A and θ^B are constants. In other words, an isothermal binary system can be characterized by a relaxation *rate* $1/\tau$ that is a linear function of the local number densities of the two species. This model allows the pure fluids to have different viscosities. The Boltzmann equations for A and B are coupled through τ and also through the barycentric velocity $\mathbf{u}$ that enters the equilibrium distribution function.

We have used the method of moments of Grad³⁵ to determine the kinematic viscosity ν and the chemical diffusivity D of this model. The results are³⁴

$$\nu = \frac{n\tau kT}{\rho} \quad (17)$$

and

$$D = \frac{\rho\tau kT}{m^A m^B n} \quad (18)$$

where $\rho = \rho^A + \rho^B$, $n = n^A + n^B$ and τ is given by Eq(16).

We have done some preliminary testing of FDLB simulations of this model for a binary ideal gas diffusion couple whose species have a mass ratio $m^1/m^0 = 0.9/1.1$. This is illustrated for the geometry of Figure 3. Even in strictly zero gravity, there is a non-Boussinesq barycentric velocity, as illustrated in Figures 4 and 5, but the resulting diffusion profiles are practically one-dimensional, as illustrated in Figure 6.

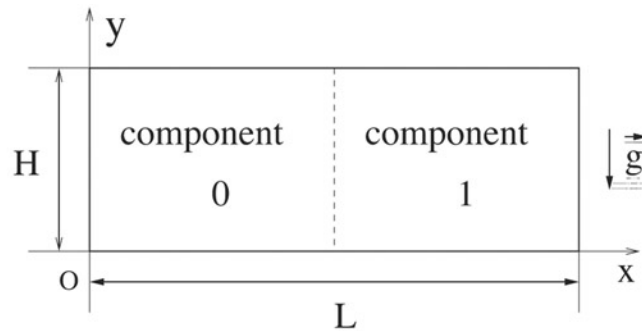


Figure 3. Geometry of diffusion couple ($H = L/5$) with heavy gas (relative mass 1.1) on the left and light gas (relative mass 0.9) on the right. Since the density depends on composition, there is a non-Boussinesq barycentric velocity, as illustrated in Figures 4 and 5, even in strictly zero gravity.

As can be ascertained approximately from the law of atmospheres, gravitational settling in gases, even for Earth's gravity g_E is quite negligible for samples of laboratory size (for these simulations, $L = 3.3$ cm and $H = 0.67$ cm). Moreover, the ratio of the compositional Rayleigh number of a gas to that of a liquid is typically 10^{-5} due to differences in kinematic viscosity (factor of 10^{-1}) and diffusivity (factor of 10^{-4}). Therefore, relative to a liquid, there is negligible buoyancy-driven convection in a gas during interdiffusion.

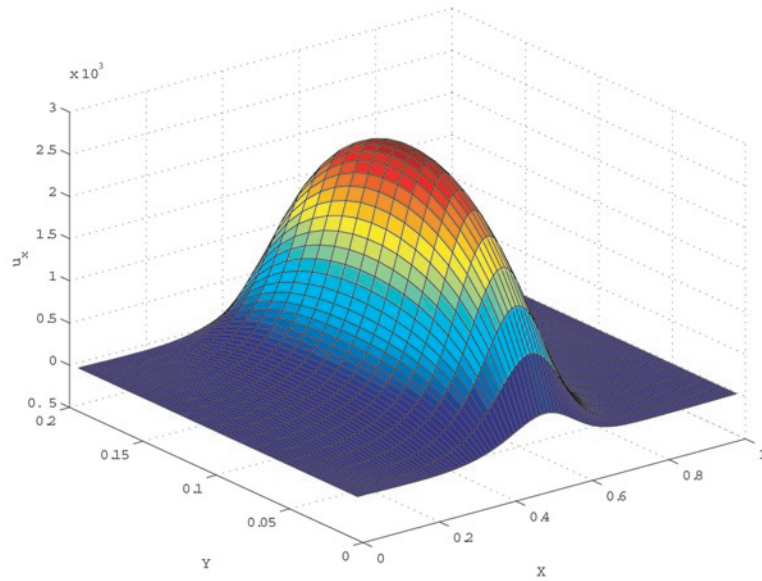


Figure 4. Component of the barycentric velocity in the x direction as a function of x and y for the diffusion couple depicted in Figure 3 for strictly zero gravity. The main flow is in the x direction due to density change during diffusion and non-Boussinesq flow.

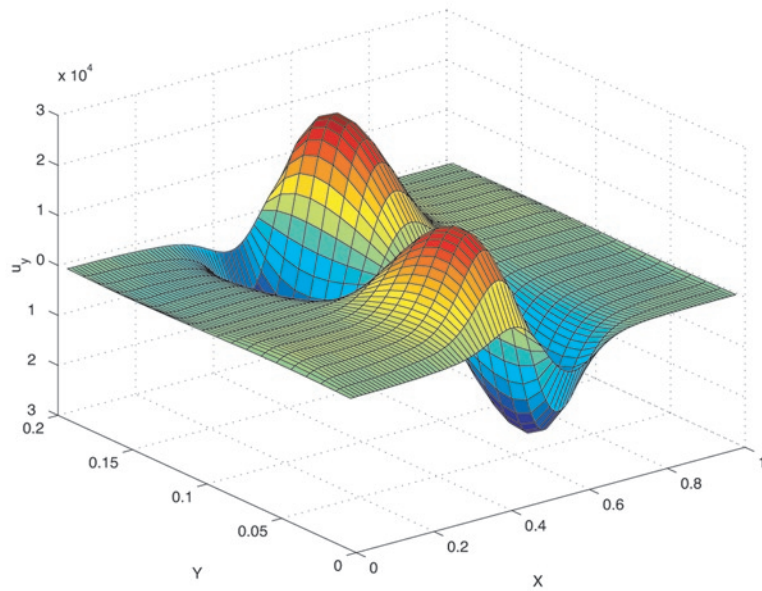


Figure 5. Component of the barycentric velocity in the y direction as a function of x and y for the diffusion couple depicted in Figure 3 for strictly zero gravity. There is flow in the y direction because of two counter-rotating cells needed to satisfy the no-slip conditions on the container walls.

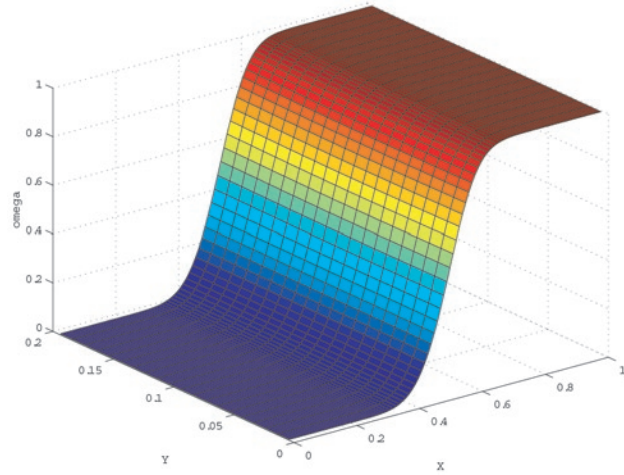


Figure 6. FDLB simulation of the mass fraction ω of the light species in strictly zero gravity in a binary gas diffusion couple for a 20% difference in species mass. Although there is a non-Boussinesq barycentric velocity, as depicted in Figures 4 and 5, the diffusion profile is practically one-dimensional.

We can, however, simulate *gravitational settling* during diffusion in a binary ideal gas at atmospheric pressure by pretending that it is in artificially high gravity $g = 10^4 g_E$. An example is shown in Figure 6 and is in agreement with the approximate (from the law of atmospheres) formula

$$\omega(x, y, t) = \omega(x, t) [1 - \omega(x, t)] \left(\frac{y - H/2}{y_0} \right) \quad (19)$$

where $\omega(x, t)$ is the mass fraction in zero gravity and $y_0 = kT/(m^0 - m^1)g \gg H$.

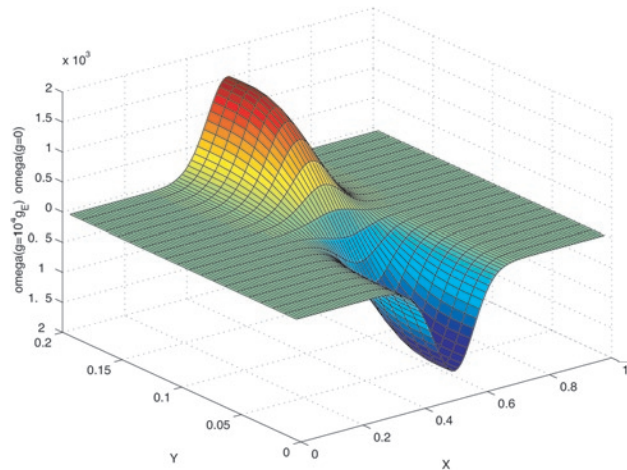


Figure 7. FDLB simulation of the difference $\Delta\omega$ of the mass fraction of the light species with and without gravity in a binary gas diffusion couple for a 20% difference in species mass. Rising of the light component and settling of the heavy component is confined to the zone of interdiffusion and can be described approximately by Eq(19).

Finally, we have begun to use the LB model to investigate the no-slip boundary condition for Poiseuille flow in a channel. For diffuse reflection from container walls, we study this problem as a function of the Knudsen number, which is the ratio of the mean free path to the system size. For small Knudsen number, LB simulations yield the classical parabolic velocity profile characteristic of the no-slip condition. But for large Knudsen number, the LB simulations yield a flat profile more nearly characteristic of “plug flow” and the no-slip boundary condition is violated. This is in agreement with the general expectation that for large Knudsen number, the mean free path is sufficiently large compared to the system size that the molecules do not “see” the walls of the container locally.

Conclusions

We have shown that various finite difference schemes used to solve the LB equations lead to different apparent (effective) viscosities. These apparent viscosities are the sum of a physical viscosity (the true viscosity) and a specious numerical viscosity (a false viscosity that depends on the computational scheme and parameters such as spatial and temporal grid sizes). By means of analysis of the finite difference equations, we have worked out formulae, Eqs(7-9), for these specious numerical viscosities and have performed numerical LB simulations that verify these results. We have formulated a new LB model for a binary fluid based on a split collision term that accounts for collisions of like and unlike particles. This results in a relaxation rate Eq(16) that is linear in the densities of the species of the binary fluid. The resulting kinematic viscosity and diffusivity are given by Eqs(17,18). We have done some preliminary testing of FDLB simulations of this model for a binary ideal gas diffusion couple. The results demonstrate non-Boussinesq flows and gravitational settling. Future simulations will deal with FDLB models that pertain to liquids, where diffusion is so relatively slow ($D \ll v$) that convective mixing takes place, even for low gravity $g \ll g_E$, during the diffusion process. This will involve the use of LB models in which there are strong interactions among particles.³⁶⁻³⁹ Finally, we have begun to use the LB model to investigate boundary conditions at container walls. These results need further study and could be important for aerodynamics.

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INFLUENCE OF PROCESSING CONDITIONS ON THE LOW TEMPERATURE PROPERTIES OF GLASSES

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Introduction

Microgravity has been shown to offer a unique environment for producing silicate¹ and chalcogenide² glasses of exceptionally low crystallinity and high homogeneity. An Earth-based method that has been shown to produce glasses with quality approaching that in microgravity, suppresses heterogeneous nucleation by levitating the melt on a film of gas, and thereby eliminates contact with the container walls³. This method is called gas film levitation (GFL).

Microgravity and GFL glass processing techniques are important for the understanding of the properties of glasses for two reasons. First, glasses known as fragile^{4,5} have a much higher tendency to crystallize than their stronger counterparts. Varying levels of crystallinity, especially in the fragile glasses, may obscure the low temperature anomalies known to occur in glasses⁶. Secondly, because of the non-equilibrium structure, the cooling rate may directly influence the low temperature properties. Since microgravity and GFL processing suppress bulk crystallization, these tools are key to resolving the influence of the high temperature properties of glasses on the low temperature ones. At the same time, by suppressing crystallization, a wider range of cooling rates is possible and a systematic analysis of the effect of cooling rate on the glassy properties can occur.

The presence of very low temperature anomalies in glasses was first demonstrated by Zeller and Pohl⁶ in 1971 in measurements of the specific heat and thermal conductivity below 1K. In 1972, these anomalies were characterized by the phenomenological two-level system (TLS) model proposed by Phillips⁷ and independently by Anderson *et al*⁸. The model postulates that because of the structural irregularity of an amorphous solid, there exist two possible tunneling configurations for an atom or group of atoms, resulting in an energy splitting. A typical density of TLS is about 10¹⁸/cm³.

An important signature of the presence of the distribution of two level systems (TLS) is the mm-wave absorption. Because this absorption varies with the thermal population difference of the two energy levels, there is a characteristic temperature and frequency dependence to the resulting feature⁹. The absorption coefficient is

$$\alpha_{res}(\omega, T) = \frac{4\pi^2 \bar{P} \mu_b^2}{3\sqrt{\epsilon} c} \left(\frac{\epsilon + 2}{3} \right)^2 \omega \tanh(\hbar\omega / 2k_B T) \quad (1)$$

where $\bar{P}$ is the density of TLS that couple to the electric field, μ_b is the electric dipole moment linking the two levels, ϵ is the real part of the dielectric constant of the material, c is the velocity of light, and the term

Keywords: glass, TLS, low temperature anomalies, fragility, levitation, new research

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in brackets represents the local field correction. The tanh function then describes the relative Boltzmann population of the two levels.

Despite the apparent success of the TLS model over the past thirty years, the fundamental question of the source of the universality of the tunneling behavior in such a diverse range of glasses from simple to network forming to polymers remains a mystery¹⁰. At the center of this puzzle is how changes in the structural disorder of a glass affect the presence of TLS. Work on amorphous ice has shown that different amorphous structures can have very different densities of optically active TLS, yet most glasses appear very similar¹¹. In fact, attempts to correlate TLS behavior with glass dynamics have come to differing conclusions^{12, 13}.

A significant experimental parameter may be the non-uniformity in the processing conditions of the samples. We have built a GFL furnace to begin testing this possibility by reprocessing various glasses. By controlling the heating and cooling rates of a soda-lime silica glass sample we are able to vary the dynamics at the glass transition while suppressing crystallization. Our initial results show systematic deviation in the far infrared TLS absorption of the slow-cooled levitated samples from that of the quenched precursor. These results show that processing can influence the low temperature glass behavior.

Experimental Setup

GFL Furnace

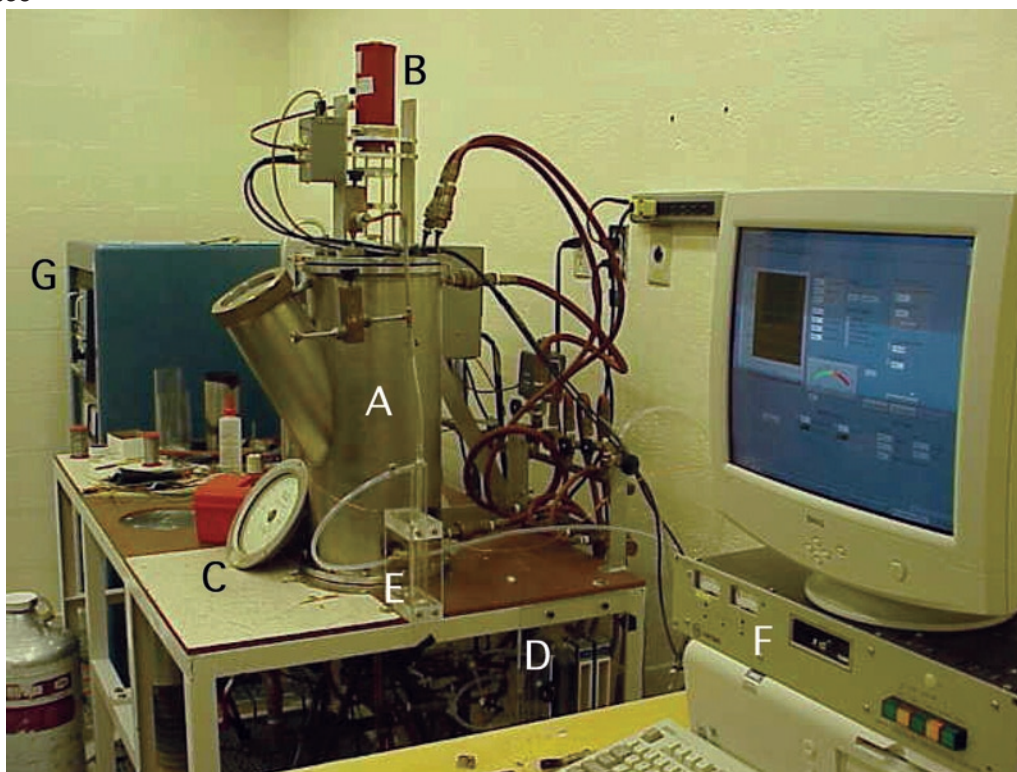


Figure 1. The main components of the gas film levitation system.

Figure 1 identifies the major components of the computer-monitored GFL furnace system. The central component, item A, is the evacuable water-cooled furnace container with viewing port. The furnace is located on a table covering various vacuum, electrical, water and pump lines. Inside the furnace chamber

are the graphite heater element, the graphite crucible and holder, and the thermocouple. Outside are the mount and optics for an infrared (IR) thermal detector (item B). The IR method for measuring the sample temperature and its rate of change is particularly important since the sample is completely isolated from its surroundings during levitation. Both the sample temperature (IR thermal radiation detector) and crucible temperature (thermocouple) are continuously monitored with a computer (item F). Items (C) and (D) identify the main pressure gauge, and the pressure regulation and gas flow meters for the system respectively. When fluorine gas is involved, a NaOH bubbler (item E) is activated to convert it to NaF. Finally, item G identifies the high current AC power supply for the furnace heater element.

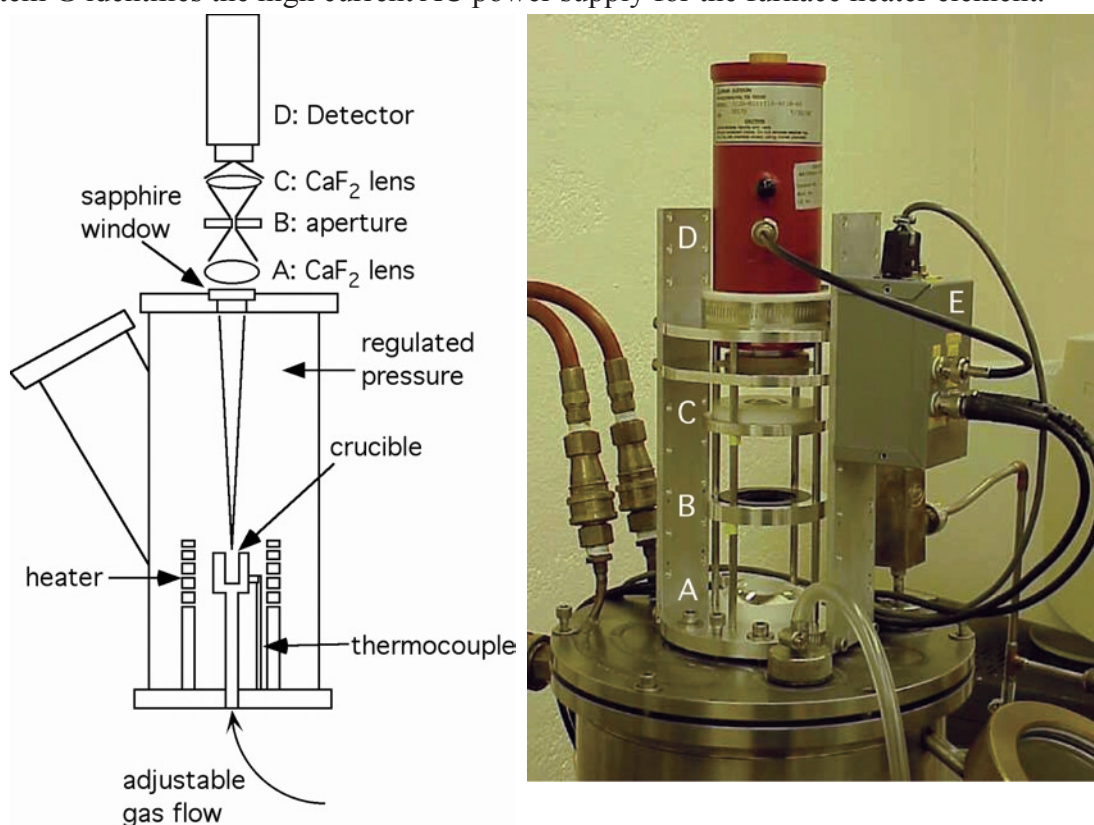


Figure 2. (a) Schematic drawing of the GFL furnace and the IR Temperature measuring optics.
(b) Physical layout of the IR calorimeter.

The detailed assembly of the inside of the furnace, including the placement of the heater, crucible, thermocouple and IR optics is shown in Figure 2(a). The graphite heater element is a high current resistive heater that can achieve controlled crucible temperatures in excess of 1400°C by conduction and/or radiation. The current to the heater is supplied by a PC controlled AC power supply (see Figure 1, item G) that can operate at up to 210V and 90A. The crucible can also be monitored visually from the side port.

The temperature of the crucible holder (see Figure 3a) is monitored by direct contact to either a chromel-alumel (K-type) thermocouple up to 1200°C or a platinum-rhodium (B-type) thermocouple up to 1500°C as needed. Further temperature monitoring is done with a liquid nitrogen cooled IR detector with confocal CaF₂ optics that remotely detects the temperature of the glass melt by the intensity of thermal IR radiation. The confocal focusing optics makes possible the rejection of the thermal radiation from both the heater and the crucible with respect to the glass sample radiation itself. This dual temperature measurement allows the GFL furnace to work simultaneously as a calorimeter.

Figure 2(b) pictures the actual physical layout of the IR calorimeter sketched in Figure 2(a) where the items A, B, C and D have been identified. Item E is the detector amplifier. In order to convert the IR thermal intensity signal into an absolute temperature for the calorimetric measurement, the detector must be calibrated.

Calibration is achieved by running the furnace at a constant rate from room temperature to 950°C and back down again at the same rate. The IR intensity on heating and cooling is averaged and the inverse trace is calculated and smoothed to give a calibration function. Finally, the sample emissivity is accounted for by scaling the IR temperature to match the thermocouple temperature when the sample is in place at a known temperature.

Sample Levitation

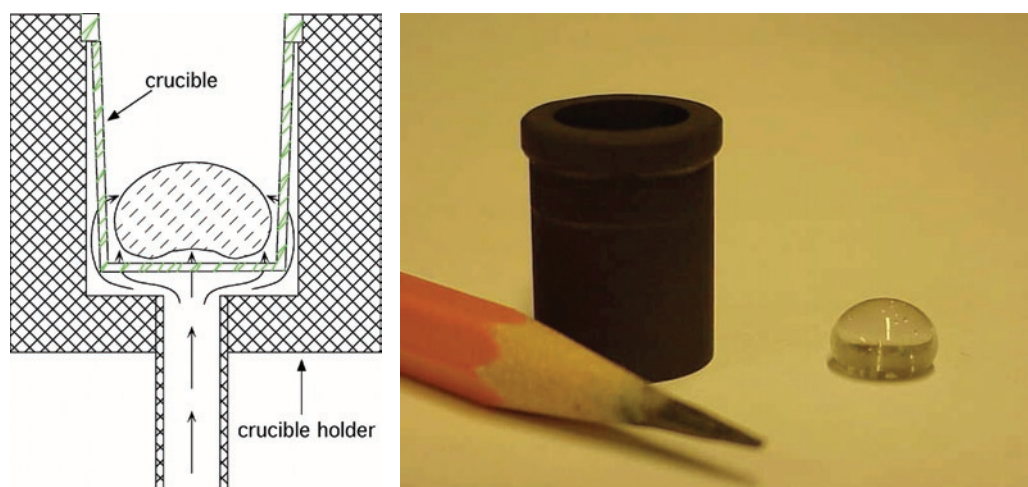


Figure 3. (a) Schematic drawing of the gas levitation details for this system. (b) Crucible and a small GFL produced soda-lime silica glass sample.

The levitation geometry is sketched in Figure 3(a) where the crucible and crucible holder provide the necessary gas flow arrangement. The inner cylindrical crucible is made of porous graphite with a 0.025" wall at a 2° angle. The angle of the wall insures easy extraction of the sample after cooling and reuse of the crucible. Various crucible designs have been tried such as the flat-bottom one shown, V-shaped and hemispherical. The V-shaped and hemispherical shapes produce a more evenly rounded bottom in soda-lime silica glass than the dimpled shape produced by the flat one shown in Figure 3(a). For the much less viscous Zirconium-Barium-Lanthanum-Aluminum-Sodium (ZBLAN) Fluoride glass only the V-shaped and hemispherical holder successfully achieved levitation. Levitation is more difficult in ZBLAN because its high density and low viscosity require a much lower flow to prevent the melt from becoming unstable, touching the crucible and irretrievably wetting the surface.

The levitation gas is ultra high purity argon that is flow regulated through the crucible with pressure regulation at the tank as well as in the furnace chamber itself. This allows precision control of the environment around the sample throughout the temperature range of the furnace (about 1450°C). The pressure of the furnace chamber can be varied from a low of 1×10^{-4} Torr with a diffusion pump to a high (850 Torr) above atmospheric pressure, with active regulation at pressures above 50 Torr.

The photograph in Fig 3(b) shows an actual crucible and a small (0.53g) soda-lime silica sample produced with this GFL technique. Several sets of crucibles and holders have been machined, with different shapes and for silica based glasses such as soda-lime silica as well as for fluoride based glasses such as ZBLAN.

IR calorimeter

The calibrated IR temperature is the instantaneous temperature of the levitated glass. The difference between the glass temperature and the crucible holder temperature, measured by the thermocouple, provides calorimetric information on the sample. Increases in the temperature difference correspond to exothermic transitions (decreases in specific heat) and decreases in the temperature difference are endothermic transitions (increases in specific heat).

The calorimetric information on the glass sample provided by the IR detector allows one to accurately identify the temperatures of thermodynamic transitions such as the crystallization or the glass transitions. Figure 4 shows the results for a ZBLAN fluoride glass. The temperature difference between the glass sample and the crucible holder is plotted versus the glass temperature during heating at 25K/min. The abscissa has been smoothed to remove the temperature jumps from that axis.

As the sample moves through the glass transition many changes take place. First there is a decrease in the sample temperature slope. This signifies the onset of the glass transition. Then the sample begins to change shape as the viscosity decreases. This results in a change in the surface scattering as well as the thermal link of the sample to the crucible as it takes on the crucible shape and begins levitating. Because of these changes, the glass transition is not a clean transition as viewed by the IR calorimeter, but is characterized by the dips and jumps evident in Figure 4.

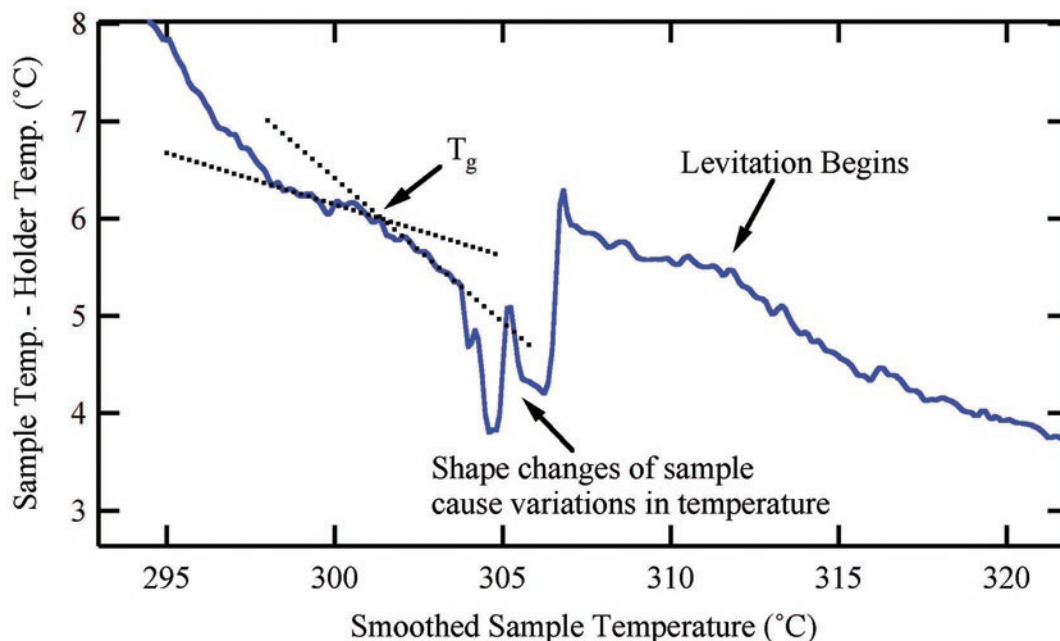


Figure 4. Example of detection of the glass transition during heating at 25K/min. of a fluoride-based glass (ZBLAN).

Sample History

The samples are well-characterized soda-lime silica glasses produced by standard melt/quench methods and provided by Corning, Inc. The composition is approximately 73% SiO_2 : 14% Na_2O : 12% CaO : 1% Al_2O_3 for all samples used in this work.

A sample of levitated soda-lime silica glass was typically processed in the following way. First, the furnace chamber was baked at 1200°C for 15 minutes without a sample at $\sim 10^{-4}$ Torr of pressure. The chamber was then filled with UHP Ar gas and the sample quickly placed into the crucible. The chamber was then re-pumped to 10^{-4} Torr and heated to 250°C for 15 min. At that point about 700 Torr of Ar was added to the chamber with active regulation. The sample was ramped at 50K/min. to 550°C for 10 min. and the levitation gas was turned on. The sample melted during heating at 50K/min. up to 950°C . As it took on a rounded lens shape, it began levitation. After 10 min. at 950°C , the sample was cooled. This could be achieved by turning off the heater (quenching) achieving $\sim 30\text{K/min.}$ at 600°C , or by controlled cooling at rates down to 5K/min. The resulting sample was typically lens shaped. It was then cut with a diamond wheel using waterless lapping oil as a lubricant and polished with fine grit abrasive paper to optical quality.

IR Spectrometer

The far-infrared measurements were carried out in a liquid helium cooled cryostat that can achieve sample temperatures from 1.4K-140K. The spectrometer is a lamellar grating interferometer with a mercury arc lamp source. The detector is a ^3He cooled germanium bolometer operating at 0.3K.

Experimental Results

Figure 5 shows a plot of the difference absorption between a given temperature and the reference temperature of 1.5K for the as-received soda-lime silica glass. Note the characteristic TLS decrease in absorption with increasing temperature up to about 7K, the highest temperature shown. Above 7K, the absorption begins to increase because of additional relaxation processes.

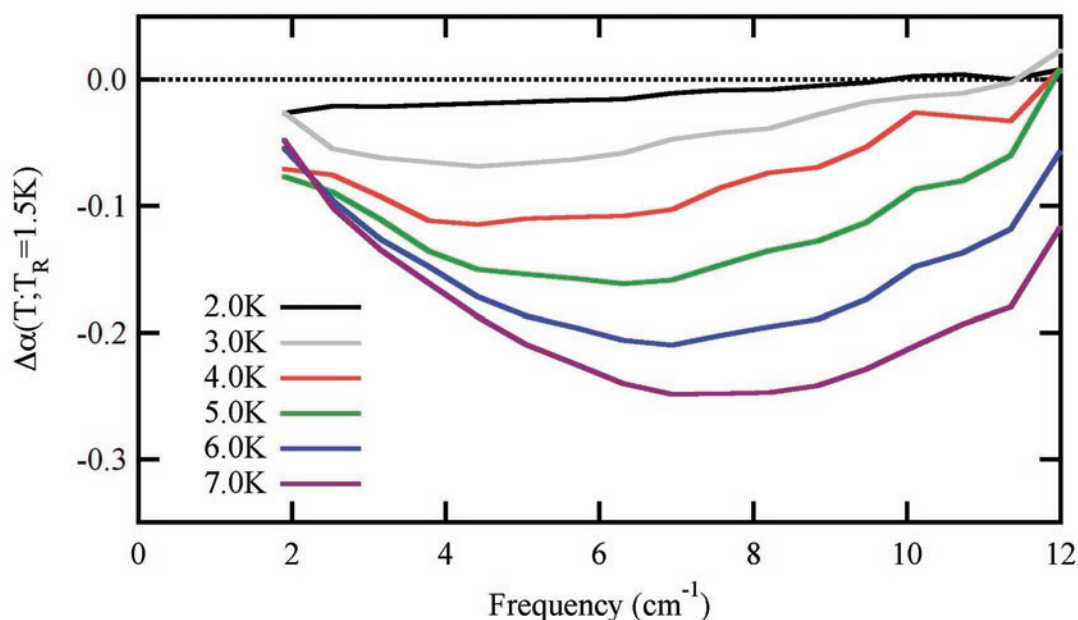


Figure 5. Characteristic TLS bleaching effect with an increase in temperature for as received soda-lime silica glass.

Figure 6 shows a plot of the negative absorption coefficient difference, $-\Delta\alpha$, versus the difference in population factors for two glass samples. The solid lines are given by Eq. 1 at several frequencies. In the as received sample (a), there is an excellent fit all the way up to 7.0K for all frequencies in the range, demonstrating the quantitative dependence of the far-infrared absorption on the TLS population factor.

But in the levitated and slow-cooled samples (Figure 6b), the difference absorption deviates markedly from the as received sample. At frequencies above $\sim 5\text{cm}^{-1}$ there is a large increase in $-\Delta\alpha$, while at lower frequencies the difference absorption decreases. At the same time the relaxation-like absorption increased, evident in the turn-over from linear behavior at higher temperatures. Note that for the levitated samples, only the lowest three points (2.0-4.0K) were used in the fit because of the increased relaxation-like absorption.

Figure 7 shows the weighted spectral density (WSD) of TLS, $\bar{P}\mu_b^2$, found from the slope of the linear fits with zero intercept shown in Figure 6. Both of the levitated samples show a distinct difference from the as received sample with an increase in WSD above a few wavenumbers and a decrease in WSD below that point. At the lowest frequencies the fits are linear but not at the higher frequencies as demonstrated by the smaller error bars.

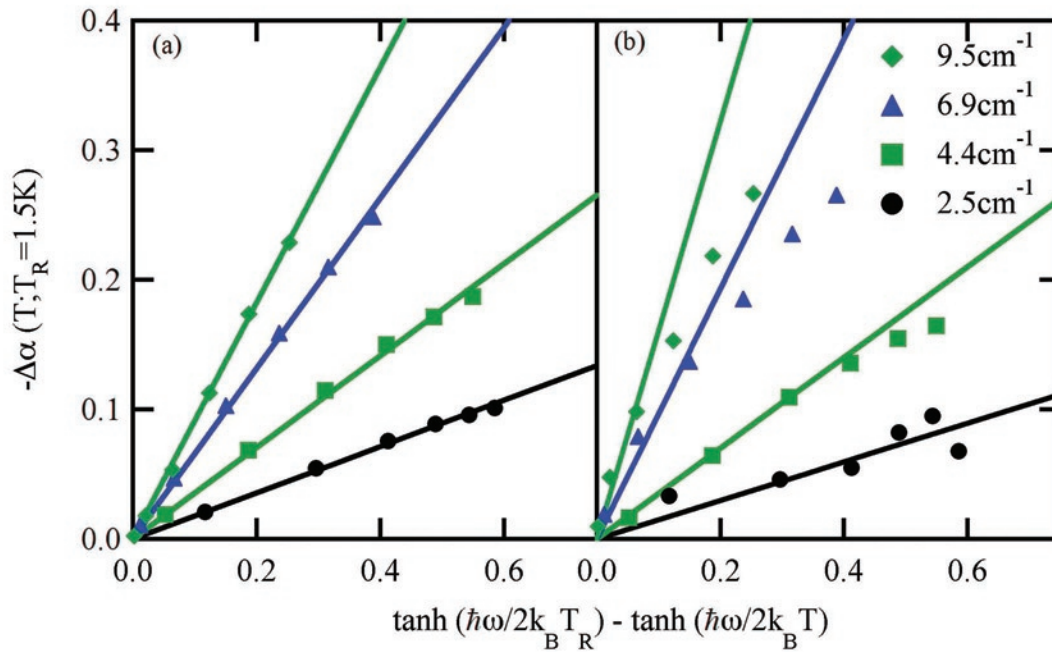


Figure 6. Fits to the difference absorption for (a) as received soda-lime silica glass and (b) levitated and cooled at 5K/min. soda-lime silica glass.

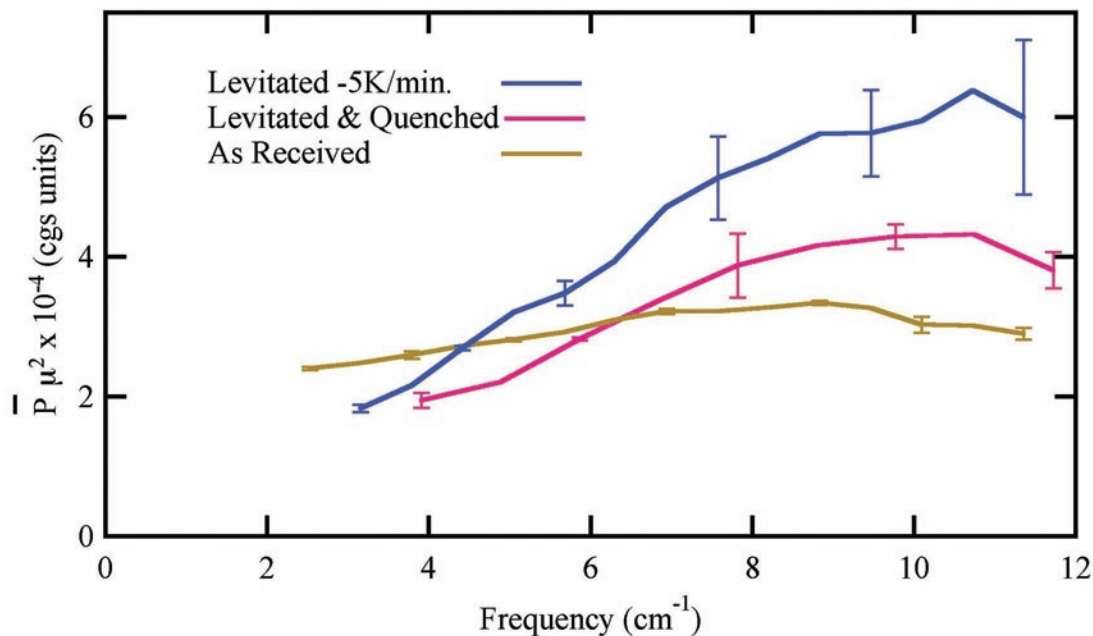


Figure 7. Weighted Spectral Density of States for the as received and GFL processed soda-lime silica glass samples studied.

Discussion and Conclusions

By levitating several soda-lime silica glass samples and cooling at a controlled rate through the glass transition our preliminary results show a qualitative difference in the far infrared absorption TLS temperature dependence. There is a shift in the density of TLS with decreased low frequency absorption and an increase at higher frequencies for the levitated samples. In addition the relaxation-like contribution to the absorption in this spectral region also appears increased.

In conclusion, initial results indicate that controlled GFL reprocessing of a network glass such as soda-lime silica at high temperature does modify the characteristic low-temperature glass dynamics. Systematic investigation of these changes promises to lead to a deeper fundamental understanding of glass dynamics. At that point, the high quality glasses producible in microgravity will be an important next step.

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UNDERCOOLING OF FERROMAGNETIC MELTS

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We have studied the undercooling of Pd-Co melts below their ferromagnetic Curie points. We have developed a model for including the magnetic contribution to the energy of formation of the alloy crystal nucleus from a liquid alloy of a different composition. The results are in good agreement with the measured composition dependence of the maximum attainable undercooling.

Keywords: undercooling, Pd-Co, ferromagnetic, alloy, new research

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DYNAMIC BIAXIAL FLEXURAL STRENGTH OF THIN CERAMIC SUBSTRATES

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1. Introduction

Thin ceramic sheets are widely used in engineering applications in modern industry. Electrically insulating thin sheets are used for electronic substrate applications in nearly all semiconductor products. Ceramic membranes are used as molecular filters in fuel cells and solid oxide electrolyzers for oxygen generation.¹ Development of high-reliability substrate materials inevitably requires the accurate characterization of the mechanical properties of those materials that have superior potential in their physical and electrical properties.

The solid oxide electrolyzers are typically made by a tape-cast process. After sintering, the products are usually in the form of thin sheets. The thickness of these sheets is typically 0.5 mm or less in engineering applications. However, the commonly used testing techniques for strength evaluation, tensile tests and three- and four-point bending tests²⁻⁴ require a specimen that is thicker than 2 mm, which makes them incompatible with the geometry of thin, tape-cast sheets. The strength of brittle materials such as ceramics and semiconductors depends significantly on specimen size and loading conditions.^{5, 6} The loading conditions in service on the electronic substrates and the solid oxide electrolyzers, with a thickness of much less than 2 mm, often involve multiaxial bending instead of simple tension or bending.

To obtain strength data under multiaxial bending, the American Society of Testing and Materials (ASTM) standardized a piston-on-3-ball method for the biaxial flexural strength of ceramic substrates.^{7,8} In such a test, a thin ceramic sheet is placed on three balls sitting 120° apart on a 25.4-mm-diameter circle. A piston pushes at the center of the circle from the other side of the ceramic sheet, thus producing a biaxial flexural loading condition. For the loads to be more evenly distributed on the ceramic sheet, it has been proposed to replace the three supporting balls by a ring. Also, the piston could be replaced by a ball, a smaller ring, or simply pressure, resulting in new designs of the biaxial flexural testing configurations: ball-on-ring, ring-on-ring, and pressure-on-ring.⁹ The ring-on-ring¹⁰ configuration was the focus of a collaborative Japan-United States effort on development of low-cost aluminum nitride materials.¹¹

Besides multiaxial bending, these thin ceramic sheets may be subjected to dynamic loading. Electronic substrates experience shock and vibration loading in the event of a drop. It is important to understand the mechanical response of the substrates under such dynamic loading conditions to improve designs for better drop-tolerances. A solid oxide electrolyzer on a spacecraft has to survive impact and vibration during launching from Earth and landing on other planets in order to produce oxygen *in-situ*, which is critical to return missions and human space exploration. It is mandatory to ensure the structural integrity of the electrolyzer over the duration of the entire space mission, which also calls for reliable multiaxial strength data under dynamic loading conditions. Unfortunately, there is a lack of experimental techniques that can

Keywords: biaxial, strength, dynamic, ceramic, stress-rate, ISRU

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provide such critical data for the thin and brittle sheets of materials. In this paper, an experimental method is presented that can determine the dynamic biaxial flexural strength. This new technique is based on a quartz-crystal-embedded split Hopkinson pressure bar¹² and the piston-on-3-ball testing configuration. The desired dynamic loading rates can be controlled under laboratory conditions. The range of loading rates from which valid data can be obtained is analytically determined. Using this new technique, the loading rate effects on the biaxial flexural strength of rupture of 8 mol% yttria stabilized zirconia (8YSZ) thin sheets were determined.

A material model is necessary to obtain an insight into the dynamic strength behavior of ceramic materials. Although material models have been proposed to describe the dynamic constitutive behavior of brittle materials under constant strain-rate loading conditions, few efforts were found to explain such dynamic behavior under constant stress-rate loading, which is the loading condition for many dynamic experimental techniques, such as this new dynamic piston-on-3-ball experimental technique, and is significant in practical use. In this paper, a new model for dynamic strength under constant stress-rate loading for brittle materials is developed based on the concept of cumulative damage. The parameters in this model are identified using an overall least squares curve-fitting technique for all the experimental results on pure and doped ceramic material 8YSZ thin sheets at different loading stress-rates, thus avoiding the massive requirements on experimental data that are neither economical nor practical to obtain. The model is found to give a good description of the dynamic constitutive behavior of brittle materials.

2. Dynamic piston-on-3-ball experimental technique

In order to maintain the same experimental conditions, except for the loading rates, the test sections of both the quasi-static and dynamic experimental facilities are identical - a standard piston-on-3-ball setup. The configuration of the dynamic piston-on-3-ball method is shown schematically in Fig. 1.

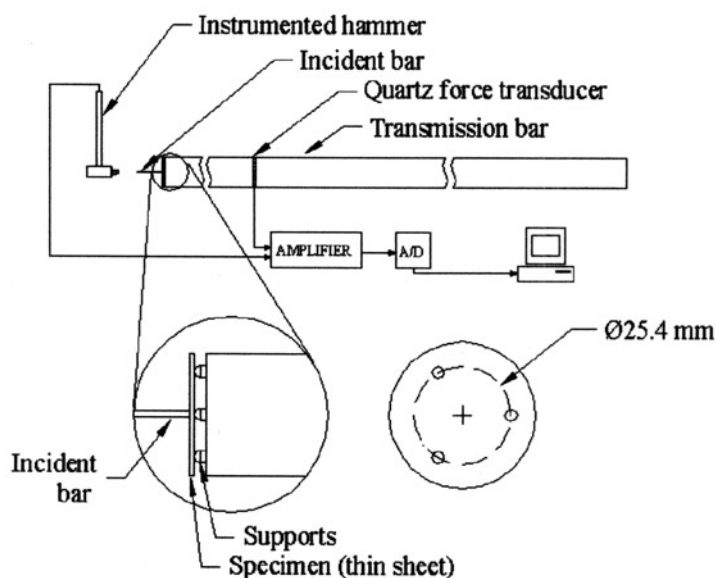


Figure 1. A schematic of the dynamic piston-on-3 -ball setup.

The working principle of the new method is similar to that of a split Hopkinson pressure bar (SHPB).¹³

¹⁴ An SHPB test is the same as a quasi-static compression test except for the loading rates. Similarly, the dynamic piston-on-3-ball test is the same as its standard quasi-static counterpart except for the loading

rates. In the experimental setup shown in Fig. 1, a PCB impact hammer (model 086C01), which can output the impulse force signal by its embedded force transducer and adjust the impulse shape (loading rate) by applying different hammer tips, is used as the dynamic load generator. The incident bar is made of stainless steel with a diameter of 1.60 mm and a length of 80 mm. The thin specimen is supported by three 3.18-mm-diameter ball bearings. All of the parameters associated with the piston-on-3-ball setup are the same as those suggested in the ASTM standard F 394-78.⁷ The transmission bar is made of a 32-mm-diameter 7075-T6 aluminum alloy bar with a Valpey-Fisher X-cut quartz crystal disk of the same diameter embedded in the middle of the bar about 560 mm from the end close to the specimen to directly measure the time-resolved transmitted force. This quartz-crystal-embedded transmission bar technique can significantly increase the signal-to-noise ratio (SNR) during an SHPB test of a weak material without affecting the wave propagation.¹² A National Instrument NI6110 A/D board, whose sampling rate per channel can be up to 5 MS/s, is used to sample the force signals from the hammer and quartz. A computer program developed using LabVIEW 6i is used to control the sampling processes during experiments.

The test procedure for the dynamic piston-on-3-ball experiment is similar to that of an SHPB test.¹³ An impulse load is applied on the center of the ceramic substrate specimen by the hammer through the incident bar. Part of the loading pulse is then transmitted through the specimen to the transmission bar. The time-resolved impulse forces in the hammer and the transmission bar are recorded simultaneously. Because of the wave propagation effects, the force signal from the transmission bar possesses a phase delay to the force signal from the hammer. The specimen is broken when the impulse force applied by the hammer reaches a high enough amplitude. The impulse peak and the loading rate can be determined from the recorded signals. Once the load peak is determined, the biaxial flexural strength, σ_F , at the center of the specimen surface in tension can be calculated using Eq. (1) derived by Kirstein and Wooley¹⁵ for quasi-static experiments, which requires the forces on both sides of the ceramic substrate to be in equilibrium.

$$\sigma_F = -\frac{3}{4\pi} \frac{P}{d^2} \left\{ \left[(1+\nu) \ln \left(\frac{r_2}{r_0} \right)^2 + \left(\frac{1-\nu}{2} \right) \left(\frac{r_2}{r_0} \right)^2 \right] - \left[(1+\nu) \left(1 + \ln \left(\frac{r_1}{r_0} \right)^2 \right) + (1-\nu) \left(\frac{r_1}{r_0} \right)^2 \right] \right\} \quad (1)$$

where P is load peak causing fracture, ν Poisson's ratio, r_0 radius of specimen, r_1 radius of support circle, r_2 radius of loading area, and d specimen thickness at fracture origin. The load peak from the hammer is always higher than the force peak from the quartz signal because the specimen failure signal needs time to propagate through the incident bar back to the hammer. Therefore, the biaxial flexural strength of the specimen should be evaluated using the signal recorded by the quartz force transducer in the transmission bar.

To obtain the dynamic material strength data without the effects of inertia, which is commonly associated with impact loading, the forces on both sides of the specimen must be nearly the same during a dynamic experiment. To examine if the specimen is in dynamic force equilibrium, the impulse force histories from both the hammer and the transmission bar are recorded; the loading rates can then be calculated from these two force records. The specimen is considered to be in dynamic equilibrium if these two loading rates are nearly equal to each other before the specimen is broken. When the loading rate exceeds a certain level, it will be impossible to achieve dynamic force equilibrium. As discussed in the following, this sets the upper limit of the loading rate for this experimental method.

Similar to the case of understanding the valid strain rate range in SHPB experiments on ceramics,¹⁶ it is important to know the limits of the loading rate for valid results on biaxial flexural strength. The loading

rate and the frequency components of a force pulse can be determined approximately by its amplitude and duration. To determine if a specific loading profile can produce valid data, it is necessary to determine the first resonant frequency of the specimen within the specific boundaries of the experimental setup. If the highest frequency component of the loading pulse is much lower than the first resonant frequency of the specimen, the specimen is approximately in its equilibrium state. Furthermore, if the loading rate is nearly constant, the brittle specimen will deform at a nearly constant velocity, which eliminates the inertia effects. To study the problem of specimen dynamic equilibrium, the experimental configuration is modeled as a multi-body dynamic system as shown in Fig. 2.

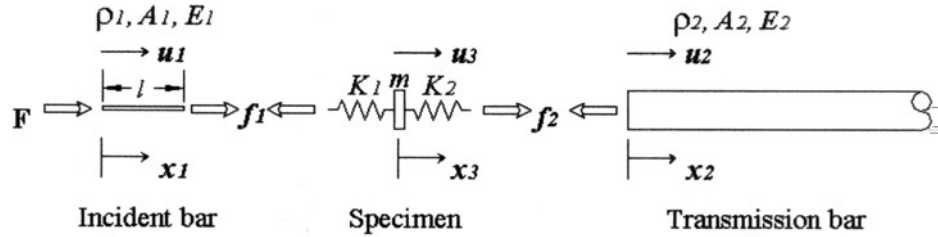


Figure 2. Free-body diagrams of the analysis model.

In this model, the ceramic substrate specimen is modeled as a single-degree mass-spring system with mass m and elastic constants K_1 and K_2 because only the frequencies under the first mode of the disk are concerned. The elastic constants K_1 and K_2 of the springs can be assumed to be half the elastic constant obtained from quasi-static piston-on-3-ball experiments on the ceramic substrate. The incident bar is modeled as a short longitudinal rod with length l , cross-section area A_1 , Young's modulus E_1 , and material density ρ_1 , while the transmission bar is modeled as a half infinite-length longitudinal rod with cross-section area A_2 , Young's modulus E_2 , and material density ρ_2 . The loading pulse, F , generated by the hammer is applied to one end of the incident bar. The coordinate x and displacement u with subscript l are associated with the incident bar, while those with subscript 2 are associated with the transmission bar. One-dimensional wave propagation theory is used to model the waves in the two bars.

In general, the equation of motion for a straight and constant cross-section rod is

$$\frac{\partial^2 u}{\partial x^2} - \frac{1}{c_0^2} \frac{\partial^2 u}{\partial t^2} = 0 \quad (2)$$

where $c_0 = \sqrt{\frac{E}{\rho}}$ is the bar wave velocity in the elastic rod. By using spectral analysis method¹⁷, the solution to this equation is

$$u(x, t) = \sum_{n=0}^{N-1} a e^{-i(kx - \omega_n t)} + \sum_{n=0}^{N-1} b e^{i(kx + \omega_n t)} \quad (3)$$

where $k = \frac{\omega_n}{c_0} = \omega_n \sqrt{\frac{\rho}{E}}$, N is the length of the DFT, ω_n is the angular frequency, and n is an index. The coefficients a and b are undetermined amplitudes that depend on each frequency.

The first term on the right-hand side represents a forward-moving wave and the second a backward-moving wave. In an idealized half infinite-length longitudinal rod such as the transmission bar, only a forward-moving wave exists. In a short bar such as the incident bar, waves travel back and forth and overlap each other.

Equation (3) is a general DFT solution to the longitudinal wave propagation in rods and can be applied to both incident and transmission bars. However, the second term does not exist in the transmission bar where no backward-moving waves exist. Therefore, the displacements of the incident bar and transmission bar are as follows:

$$u_1(x, t) = \sum_{n=0}^{N-1} a_1 e^{-i(k_1 x - \omega_n t)} + \sum_{n=0}^{N-1} b_1 e^{i(k_1 x + \omega_n t)} \quad (4)$$

$$u_2(x, t) = \sum_{n=0}^{N-1} a_2 e^{-i(k_2 x - \omega_n t)} \quad (5)$$

Boundary conditions must be applied to determine the coefficients a_1 , b_1 and a_2 . One end of the incident bar is subjected to the load $F(t)$ generated by the hammer. The other end is resisted by force f_1 , which is from the spring K_1 . When the bar material is linearly elastic, both forces can be related to the respective displacement gradient at the bar ends,

$$E_1 A_1 \left. \frac{\partial u_1(x_1, t)}{\partial x_1} \right|_{x_1=0} = F(t) = \sum_{n=0}^{N-1} F(n) e^{i\omega_n t} \quad (6)$$

$$E_1 A_1 \left. \frac{\partial u_1(x_1, t)}{\partial x_1} \right|_{x_1=l} = f_1(t) = \sum_{n=0}^{N-1} f_1(n) e^{i\omega_n t} \quad (7)$$

The end of the transmission bar is subjected to the force f_2 , which is the resistive force of the spring K_2 ,

$$E_2 A_2 \left. \frac{\partial u_2(x_2, t)}{\partial x_2} \right|_{x_2=0} = f_2(t) = \sum_{n=0}^{N-1} f_2(n) e^{i\omega_n t} \quad (8)$$

The lumped mass of the specimen moves according to Newton's second law,

$$f_2 - f_1 = m \frac{d^2 u_3}{dt^2} \quad (9)$$

which should vanish in an ideal dynamic experiment. In addition, the linear elasticity of the springs is described by

$$f_1 = K_1 [u_3 - u_1(l, t)] \quad (10)$$

$$f_2 = K_2 [u_2(0, t) - u_3] \quad (11)$$

These boundary conditions can be written in terms of the corresponding Fourier components as follows in matrix form:

$$\begin{bmatrix} -ik_1 E_1 A_1 & ik_1 E_1 A_1 & 0 & 0 & 0 & 0 \\ -ik_1 E_1 A_1 e^{-ik_1 l} & ik_1 E_1 A_1 e^{ik_1 l} & 0 & -1 & 0 & 0 \\ 0 & 0 & ik_2 E_2 A_2 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 1 & m\omega_n^2 \\ K_1 e^{-ik_1 l} & K_1 e^{ik_1 l} & 0 & 1 & 0 & -K_1 \\ 0 & 0 & K_2 & 0 & -1 & -K_2 \end{bmatrix} \begin{bmatrix} a_1 \\ b_1 \\ a_2 \\ f_1 \\ f_2 \\ U_3 \end{bmatrix} = \begin{bmatrix} F \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (12)$$

where U_3 is DFT component of u_3 . While these equations can be solved explicitly, an examination of the dynamic equilibrium of the specimen by means of analyzing the transfer function between f_1 and f_2 will be made here. From Eq. (12) the transfer function, $H_1(\omega_n)$, between f_1 and f_2 , which should be unity in an ideal experiment, can be solved.

$$H_1(\omega_n) = \frac{f_2}{f_1} = \frac{1}{\left(1 - \frac{m\omega_n^2}{K_2}\right) + i\left(\frac{m\omega_n}{A_2\sqrt{\rho_2 E_2}}\right)} \quad (13)$$

Since the parameters m and K_2 are determined by the material and geometry of the specimen, and ρ_2 and E_2 are determined by the transmission bar material (aluminum alloy), the only parameter that can be adjusted is the cross-sectional area A_2 of the transmission bar. Increasing A_2 can reduce the deviation of H_1 from unity. However, the choice of A_2 depends on the cross-sectional area of the available quartz embedded in the transmission bar.

Equation (13) is very illustrative in determining the highest frequency component of the force pulse that can pass through the specimen without significant dispersion. In practice, however, it is not convenient to use in judging if the specimen is in the equilibrium state, because the frequency analysis of the signal f_1 is impossible since the time history of f_1 is not available. Therefore, another tool must be devised to ensure specimen equilibrium. Equation (12) also facilitates the transfer function H_2 between F and f_2 , which is the dynamic force response at the point of the quartz force transducer in the transmission bar due to the applied load of the hammer. The time histories of both F and f_2 are available from the signal records of a test,

$$H_2(\omega_n) = \frac{f_2}{F} = \frac{2\lambda}{\gamma_1(1-\lambda^2) \left\{ \left[\frac{1+\lambda^2}{\gamma_1(1-\lambda^2)} - \frac{1}{K_1} \right] \left[1 - \frac{m\omega_n^2}{K_2} - \frac{m\omega_n^2}{\gamma_2} \right] - \frac{1}{m\omega_n^2} \right\}} \quad (14)$$

where $\gamma_1 = ik_1 E_1 A_1$, $\gamma_2 = ik_2 E_2 A_2$, and $\lambda = e^{ik_1 l}$.

The first resonant frequency of H_1 - the first resonant frequency of the specimen/transmission bar system - is definitely higher than the first resonant frequency of H_2 - the first resonant frequency of the incident bar/specimen/transmission bar system because H_1 is a subsystem of H_2 . As a result, if the hammer load is bandlimited within some frequency such that the specimen is in a dynamic equilibrium state, the input load pulse by the hammer can propagate through the specimen into the transmission bar without dispersion, *i.e.*, all of the frequency components of the input pulse can pass through with gain 1 and without phase distortion.

3. Material model for dynamic strength under high stress-rate loading

The behavior of brittle materials such as ceramics under high-speed loading has been the subject of many studies during the past. Many experiments revealed that rapidly loaded structures could bear stresses that considerably exceeded the critical levels under static loading conditions.¹⁸⁻²⁰ The most recent review of the field of dynamic failure mechanics is that of Rosakis and Ravichandran.²¹

Most existing constitutive models for high-speed loading are constant strain-rate models. In order to describe the dynamic strength behavior of brittle materials accurately, it is necessary to develop high stress-rate models, also. The importance of such models is conditioned by two circumstances. First, besides constant strain-rate loading, material tests under constant stress-rate loading are also rather routine and equally valuable to determine dynamic material behavior. For example, a split Hopkinson pressure bar (SHPB) can generate either a uniaxial constant strainrate or constant stress-rate loading condition in a specimen if the incident pulse is properly controlled.²²⁻²⁴ Many other dynamic experimental techniques,

such as the drop ball test (DBT)²⁵ and the dynamic piston-on-3-ball test, generate a constant stress-rate loading condition in the specimen. Second, in many applied problems, the substitution of the real stress velocity by some averaged value for the whole process does not lead to a significant error.²⁶

In the following, a new model is proposed to describe the dynamic strength of brittle materials under a constant stress-rate loading condition by using Tuler and Butcher's²⁷ general failure criterion based on the concept of damage accumulation. Freund²⁸ outlined Tuler and Butcher's model in the form

$$\int_0^{t_s} \left[\frac{\sigma(t)}{\sigma_w} - 1 \right]^\beta dt = C \quad (15)$$

where $\sigma(t)$ is a representative stress (such as the remote tensile stress in the case of uniaxial loading and/or the central stress on the tensile surface in the case of biaxial loading, *e.g.*, piston-on-3-ball loading), σ_w is the stress threshold for the beginning of damage accumulation, t_s is the time required for the stress to start from σ_w and to reach its maximum level, and β and C are experimentally determined material constants.

Two idealized assumptions are introduced in the development of this new model. First, the threshold stress, σ_w , is approximately the same as the strength of the same material under static loading. The dynamic strength of a brittle material always increases from its static strength with increasing strain rate as commonly observed from experiments.¹⁸⁻²⁰ Second, the dynamic strength depends only on the loading history after the stress load exceeds the static strength. This means the loading mode has no effect on the dynamic strength if the stress load is less than the static strength. This is consistent with the "weakest link" concept in fracture mechanics,²⁹ which indicates that the critical crack propagation determines the strength of a brittle material. In other words, the crack size distribution in the material bulk does not change if the applied load is under its static strength. Therefore, the initial time can be set at the point where stress load passes the static strength. The loading stress history after passing σ_w can then be expressed as

$$\sigma(t) = (\dot{\sigma}t + \sigma_w)H(t) \quad (16)$$

where $H(t)$ is the Heaviside function and $\dot{\sigma}$ is the applied constant stress-rate. Substituting (16) into (15), we obtain

$$\frac{\dot{\sigma}^\beta}{\sigma_w^\beta} \frac{t_s^{\beta+1}}{\beta+1} = C \quad (17)$$

The stress, $\sigma(t)$, increases linearly from σ_w at $t = 0$ to the dynamic strength, σ_s , at $t = t_s$ in this constant stress-rate strength model, *i.e.*,

$$\sigma_s = \dot{\sigma}t_s + \sigma_w \quad (18)$$

By eliminating t_s in Eqs. (17) and (18), we obtain

$$\sigma_s = \sigma_w \left[1 + \left(\frac{\dot{\sigma}}{\dot{\sigma}_r} \right)^{1/(1+\beta)} \right] \quad (19)$$

where the reference stress-rate, $\dot{\sigma}_r$, is defined as

$$\dot{\sigma}_r = \frac{\sigma_w}{(1+\beta)C}$$

Both quasi-static and dynamic experiments were performed on pure 8-mol% yttria stabilized zirconia (8YSZ) and six of its doped versions. The piston-on-3-ball technique, which is an ASTM standardized method, was used for the quasi-static experiments, while the newly developed dynamic piston-on-3-ball method was used for the dynamic experiments.

The specimens were made from TZ-8YSZ powder (TOSOH USA, Inc., Atlanta, GA). The powder was mixed with dopants and was then processed into a slurry with dispersant, binder, and plasticizer, and the slurry was tape-cast. Then, the specimens were laser-cut out of green sheets and sintered at 1450°C for 3 hours. The surface roughness of as-fired specimens is between 20 and 30 μm as observed with a Zeiss IM 35 inverted microscope.

The geometry of the specimen is the one recommended by ASTM F 394-78:⁷ 32 mm in diameter and 0.75 mm in thickness. An X-ray diffraction (XRD) analysis performed on the materials revealed that only the cubic phase was present in all these specimens. The surface condition of the specimens was made as close as possible to that used in practice since the intention was to obtain realistic strength data for design purposes. Therefore, the specimens used in this research had as-fired surface finishes. Under this surface condition, the test results included all the factors that had effects on the biaxial flexural strength, such as material compositions and processing parameters, in addition to surface flaws.

The model for dynamic strength at high stress-rate loading as expressed by Eq. (19) recovers the strength at the quasi-static state as the loading rate approaches zero. In other words, this model covers the stress-rate range from zero, which is not the case for other models in the literature. Denoual's high stress-rate fracture strength model³⁰ and Morozov's high stress-rate yield strength model²⁶ cover only a stress-rate range that starts at some finite value. This finite value has to be experimentally estimated for each material, causing difficulties in the application of these models in practice.

Theoretically, we need at least 30 experiments³ for each stress-rate to estimate the statistical distribution of strength results without a model. This is neither economical nor practical since a huge amount of data must be acquired by experiments. With the help of the dynamic strength model, Eq. (19), it is possible to fit all experimental data with different stress-rates together. Therefore, this method helps to reduce the minimum requirement for the number of experiments.

Table 1. Dynamic strength parameters

Ceramic Alias	Reference stress-rate $\dot{\sigma}_r$	Parameter β
8YSZ	2574	0.490
1 mol% Al ₂ O ₃ -doped 8YSZ	2589	0.414
2 mol% Al ₂ O ₃ -doped 8YSZ	2867	0.429
3 mol% Al ₂ O ₃ -doped 8YSZ	2530	0.459
10 wt% 3YSZ-doped 8YSZ	3398	0.434
20 wt% 3YSZ-doped 8YSZ	3121	0.454
30 wt% 3YSZ-doped 8YSZ	3709	0.470

4. Conclusions

An experimental technique for determining the biaxial flexural strength of thin ceramic substrates at high loading rates has been developed and verified by experiments. The loading configuration is the same as the quasi-static piston-in-3-ball experimental technique, making the high loading rate results directly comparable to the standard quasi-static results. The upper and lower limits of the loading rate range for a valid experiment with a specific specimen were analyzed.

A new model for dynamic strength under constant high stress-rate loading for brittle materials was developed based on the concept of cumulative damage. The parameters in this model were experimentally identified using an overall least squares curve-fitting technique for all the data at different loading stress-rates.

Ceramic material 8YSZ and six of its doped compositions with alumina and 3YSZ were tested using a standard piston-on-3-ball method under quasi-static loading and a newly developed dynamic piston-on-3-ball method under high stress-rate loading. The experimental results show that the new dynamic strength model for brittle materials describes both the quasi-static strength and the dynamic strength behavior appropriately.

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PARTICLE ENGULFMENT AND PUSHING BY SOLIDIFYING INTERFACES - RECENT THEORETICAL AND EXPERIMENTAL DEVELOPMENTS

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Abstract

The objective of the work on Particle Engulfment and Pushing by Solidifying Interfaces (PEP) include 1) to obtain fundamental understanding of the physics of particle pushing and engulfment, 2) to develop mathematical models to describe the phenomenon, and 3) to perform critical experiments in the microgravity environment of space to provide benchmark data for model validation. Successful completion of this project will yield vital information relevant to a diverse area of terrestrial applications. With PEP being a long term research effort, this report will focus on advances in the theoretical treatment of the solid/liquid interface interaction with an approaching particle, experimental validation of some aspects of the developed models, and the experimental design aspects of future experiments to be performed on board the International Space Station.

Introduction

The study of particle behavior at solid/liquid interfaces (SLI's) is at the center of the *Particle Engulfment and Pushing* (PEP) research program. Interactions of particles with SLI's have been of interest since the 1960's, starting with geological observations, i.e., frost heaving. Ever since, this field of research has evolved as being significant to metal matrix composite materials, fabrication of superconductors, inclusion control in steels, and many other fields. The PEP research effort is geared to understand the fundamental physics of the interaction between particles and a planar SLI. Experimental work including 1-g and μ -g experiments accompany the development of analytical and numerical models and have already been presented elsewhere^{1,2,3}.

Real-time X-ray studies of SLI interaction with a second phase, i.e., gas pores and insoluble particles, are used to investigate the influence of the thermal and solutal field on the SLI morphology and the subsequent effect on the critical velocity of engulfment and will be presented here. The modeling efforts have grown from the initial steady-state analytical model to dynamic models, accounting for the initial acceleration of a particle at rest by an advancing SLI. To gain a more comprehensive understanding, numerical models were developed to account for the influence of the thermal and solutal field, on the critical velocity of engulfment. Some of these results will be presented in the theoretical part of this paper. Current efforts are geared towards the numerical calculation of the drag force and to couple the diffusive 2-D front tracking model with a fluid flow model to account for differences in the critical velocity of engulfment in 1-g and μ -g environments.

Keywords: particle pushing, interface tracking, interface morphology, μ -g experiments

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Theoretical

The theoretical problem is to accurately track the sharp and arbitrarily shaped SL interfaces. Finding an adequate solution to this problem is an important and necessary step, because it can open new possibilities to study the micro-scale phenomena occurring during the solidification. Morphological stability, coarsening processes and SL interface interaction with gaseous or non-metallic inclusions are only a few examples of phenomena that existing numerical solidification models cannot accurately describe. Amongst the various interface tracking techniques developed to date the *boundary-fitted coordinates*^{4,5,6} and the *phase-field*^{7,8,9} methods are the most notable. However, the boundary-fitted coordinates method experiences difficulties when dealing with highly distorted interfaces. It requires remeshing as the interface changes its shape. The phase-field method can use only a simple finite-difference technique, a fixed grid and does not require remeshing. However, it is computationally intensive and produces only diffuse interfaces. In addition, the several constants and parameters involved in the model are difficult to correlate to real physical systems. Because of the weaknesses of these methods, Udaykumar and Shyy^{10,11,12} have proposed a new technique based on a finite volume formulation. The moving SL interface is represented by a discrete set of markers that are positioned at the intersection of the interface with the grid lines. In this manner, after each iteration only the interface must be reconstructed. However, the requirement of redefinition of the control-volumes near the interface considerably increases the difficulty of model implementation and makes it susceptible to numerical errors. Our new approach uses the finite-difference formulation thus eliminating the need for control-volumes redefinition at the interface. It also includes the capability to track the interface during the solidification of alloys^{13,14}.

Directional solidification of pure aluminum in the vicinity of a spherical ZrO_2 particle of radius $R_p = 22.5 \mu\text{m}$ was chosen as a first case study. The imposed solidification velocity was $V = 2 \mu\text{m/s}$ under a thermal gradient in the liquid $G_L = 7 \text{ K/mm}$. The calculations were performed on a sample of length $L = 2 \text{ mm}$ and a width W which was varied, from case to case, from 1 mm to 0.4 mm in order to test its influence on the evolution of the SL interface shape. However, no noticeable effect was observed. At the beginning of the calculations (*i.e.*, $t = 0$) it was considered that at one end of the sample a slice of $\Delta z = 10 \mu\text{m}$ thickness was in solid state and that the SL interface was perfectly planar. The center of the particle was placed at $x = W/2$ and $z = \Delta z + h_c$, where h_c is the distance between the particle center and the planar SL interface (Fig. 1).

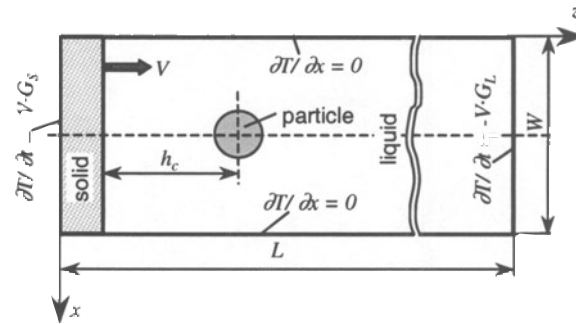


Fig. 1. The geometry and boundary conditions for the sample used in computations

Insulated boundary conditions were used on the x -direction while at the two ends of the sample constant cooling rates were considered. The cooling conditions were set such as to maintain the imposed solidification velocity, V , of the originally planar interface for the entire duration of the calculations. They were $\partial T / \partial t = -V \cdot G_L$ at the liquid end and $\partial T / \partial t = -V \cdot G_s$ at the solid end, where G_s is the temperature gradient in the solid phase.

The available analytical solution for a problem of this type¹⁵ predicts that when the thermal conductivity of the particle, k_p , is smaller than that of the liquid, k_L , the SL interface will become convex toward the particle, forming a bump as it approaches the particle. Indeed, our numerical calculations show this behavior as can clearly be observed in Fig. 2 and Fig. 3.

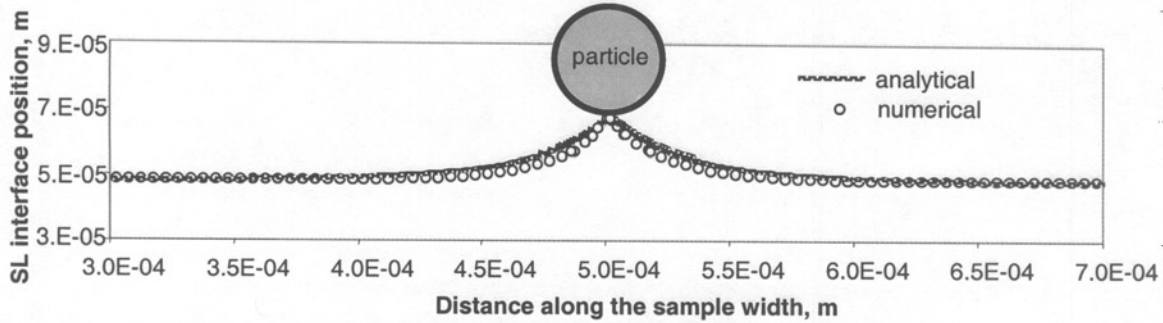


Fig. 2. SL interface shape: comparison of analytical and numerical solutions (pure Al, ZrO_2 particle $R_p = 22.5 \mu\text{m}$, $V = 2 \mu\text{m/s}$, with no Gibbs-Thomson effect)

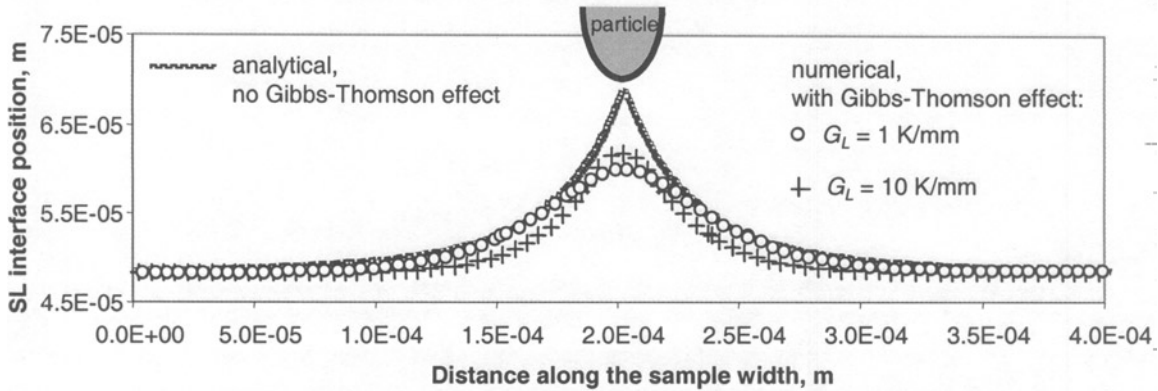


Fig. 3. Influence of the Gibbs-Thomson effect and the temperature gradient, G_L , on the shape of the SL interface (pure Al, ZrO_2 particle $R_p = 22.5 \mu\text{m}$, $V = 2 \mu\text{m/s}$). For a better view of the interface deformation non-equal scales were used on the vertical and horizontal directions, leading to the non-circular appearance of the sphere.

Fig. 2 shows a comparison between the numerical and the analytical solutions when neglecting the Gibbs-Thomson effect (*i.e.*, $\Gamma = 0$). The agreement is good, thus proving the capability of the proposed interface tracking model. In all our numerical simulations, the interface perturbation is somewhat sharper than that predicted by the analytical solution. This is mainly because of the insulated boundary conditions used at a finite distance from the particle (see Fig. 1) as compared to the analytical solution which implies that $\partial T/\partial x = 0$ occurs at $x \rightarrow \infty$.

Fig. 3 shows the shape of the SL interface when accounting for the Gibbs-Thomson effect. It can be observed that, as expected, the amplitude of the interface perturbation becomes considerably smaller as compared to the case when $\Gamma = 0$. The influence of the temperature gradient, G_L , is also shown on this figure. As G_L increases, the perturbation becomes sharper and its amplitude also increases. This implies that the perturbation develops faster when increasing G_L .

The Influence of Solute

The first test-problem that we consider in this case is the solute redistribution during the initial transient of plane front directional solidification of a binary alloy. An analytical solution to this problem¹⁷ shows that the concentration profile, $C_s(z)$, in the solidified sample can be expressed as:

$$C_s(z) = \frac{C_o}{2} \left\{ 1 + \operatorname{erf} \left[\frac{\sqrt{(V/D_L)} \cdot z}{2} \right] + \right. \\ \left. (2k-1) \cdot e^{k(k-1)(V/D_L) \cdot z} \cdot \operatorname{erfc} \left[\frac{2k-1}{2} \sqrt{(V/D_L)} \cdot z \right] \right\} \quad \text{Eq. 1}$$

where C_o is the initial concentration in the liquid sample, z is the distance measured from the beginning of the sample along the solidification direction, and erf and erfc are the error and complementary error functions, respectively.

The results shown in Fig. 4 are for Sn-0.5 at% Bi alloy at $V = 4.9 \mu\text{m/s}$ and a thermal gradient in the liquid $G_L = 17.3 \text{ K/mm}$. The numerical calculations were performed for a sample of length $L = 10 \text{ mm}$ and width $W = 20 \mu\text{m}$ using a grid size of $4 \mu\text{m}$. In order to maintain the imposed solidification velocity and temperature gradients for the entire duration of the calculations the following boundary conditions for the temperature at the two ends of the sample have been used:

$$\begin{aligned} &\bullet \quad \text{at the liquid end} & \bullet \quad \text{at the solid end} \\ \text{Eq. 2} \quad \frac{\partial T}{\partial t} &= - \left(V \cdot G_L + m_L \frac{\partial C_L^I}{\partial t} \right) & \text{Eq. 3} \quad \frac{\partial T}{\partial t} &= - \left(V \cdot G_S + m_L \frac{\partial C_L^I}{\partial t} \right) \end{aligned}$$

where $\partial C_L^I / \partial t$ represents the time change of the liquid concentration at the SL interface. Insulated boundary conditions for both temperature and concentration were used on the x -direction as shown in Fig. 1.

A good agreement between the analytical solution and the numerical results can be observed in Fig. 4. In addition, the experimental measurements of Favier *et al*¹⁶ performed on a sample solidified in micro-gravity conditions are also in good agreement with our numerical results.

With the numerical model validated against analytical solutions and experimental results for the solidification of binary alloys we can proceed to study the evolution of the SL interface shape when a foreign particle is added to the melt in front of the interface. We chose Al-2 wt% Cu for the alloy and ZrO_2 for the particle. A steady-state distribution for the solute and linear distribution for the temperature was considered as initial conditions. The boundary conditions for temperature are presented in Fig. 1. Insulated boundary conditions on the x -direction as well as on the surface of the particle were added for the solute.

While for the solidification of pure substances our numerical calculations as well as the analytical solution¹⁹ show that the solidification velocity has a negligible effect on the evolution of the SL interface near a foreign particle, this conclusion cannot be extended to solidification of alloys. The influence of the solidification velocity is shown in Fig. 5. The solute trapping in the particle/interface gap becomes more significant with the increase of the solidification velocity and therefore the depth of the concavity formed

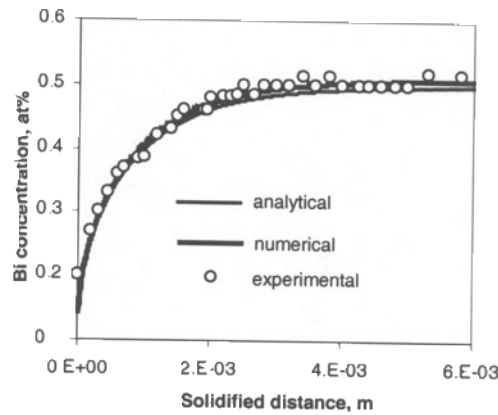


Fig. 4. Numerical predictions vs. analytical solution¹⁷ and experimental measurements¹⁸ for Bi segregation during the initial transient plane front solidification ($V = 4.9 \mu\text{m/s}$) of Sn-0.5 at% Bi on the SL interface beneath the particle will be higher at higher solidification velocity. On the other hand, when measured with respect to the flat region of the interface, the amplitude of the two humps that form on both sides of the vertical centerline is smaller at higher velocities. Thus, the solute effect becomes predominant over the thermal effect (quantified through the ratio k_p/k_L) when increasing the solidification velocity. Note that for the velocity $V = 2 \mu\text{m/s}$, used to generate Fig. 5, the stability theory²⁰ predicts that the SL interface is inherently unstable and perturbations other than induced by the presence of the particle should also appear on the interface. This is true and we have demonstrated²¹ that the present model has the capability to describe the development of such perturbations. For the case presented in Fig. 5, however, where the sample width, W , was considered of only 0.4 mm the perturbations induced by the presence of the particle override the perturbations that would have been induced by the constitutional undercooling effect alone.

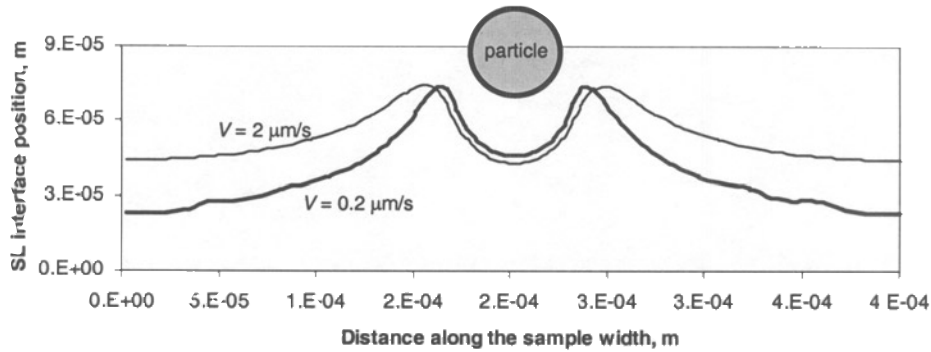


Fig. 5. Influence of the solidification velocity on the shape of the SL interface when approaching a foreign particle (Al-2 wt% Cu, ZrO_2 particle, $R_p = 22.5 \mu\text{m}$, $G_L = 7 \text{ K/mm}$)

Experimental

Ground based work

To validate the model described in the theoretical part, the dynamics of the interaction between a gas pore and a solidification front in metal alloys was observed using a state of the art X-ray Transmission Microscope. The experiments included observation of the distortion of the SL interface near a pore, real-time measurements of the growth rate and the change in shape of the porosity during interaction with an advancing SL interface in pure Al and Al-0.25 wt% Au alloy. In addition, porosity induced solute

segregation patterns surrounding a pore were also quantified with the model system Al-0.25 wt% Au alloy. Fig. 6 shows a post-solidification radiograph of a pore after engulfment by a planar SL interface. The pore has an ellipsoidal shape with a size of about 800 μm along the major axis and 660 μm along the minor axis. The growth velocity was 5 $\mu\text{m/s}$ and the temperature gradient 4.7 K/mm. The purpose of this experiment was to investigate the effect of the pore on the solutal segregation pattern. The radiograph shows that there is a strong segregation of Au around the pore just prior to engulfment. The SEM micrograph (Fig. 6b) in the inset shows that the microstructure in this area consists of eutectic colonies. The eutectic structure inside one such colony is shown in Fig. 6c. The thickness of this eutectic ‘band’ varies between 70-80 μm . The centerline microprobe scan indicates that the Au composition in this region is approximately 8.0 wt%. This is in agreement with the equilibrium phase diagram for the Al-Au system, which shows a eutectic transformation at 7.46 wt. % Au. Subsequent to engulfment of the pore, a comet tail shaped segregation pattern is clearly evident on the left of the pore (Fig. 6a).

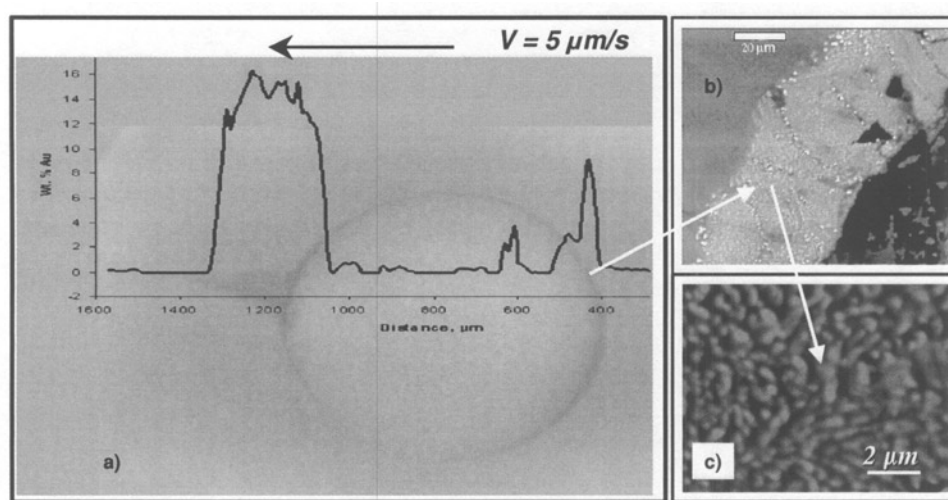


Fig. 6. Post-solidification radiograph showing segregation of Au around the porosity. Superimposed is a centerline microprobe scan.

In its current stage, the previously described model does not have the capability to account for changes of pore size and shape during the interaction with the SL interface. Therefore, only spherical pores of constant radius have been used in the present numerical modeling. Fig. 7 shows the calculated shape of the SL interface in various stages of a H_2 pore engulfment by the solid phase. The occurrence of a trough on the SL interface after engulfment is also observed. This is typical when the thermal conductivity of the particle (H_2 pore in this particular case) is smaller than that of the metallic matrix.

For the solidification of the Al-0.25 wt% Au alloy our calculations also predict that at a distance from the pore similar to that experimentally observed, the Au concentration raises to the eutectic value, as shown in Fig. 8. Fig. 9 shows a three-dimensional view of the Au concentration profile around the pore when the concentration in the pore/SL interface gap reaches the eutectic value.

At this stage, the concentration behind the pore, in the vicinity of the centerline of the sample, is smaller than in the regions away from the centerline. This is expected because the solute cannot diffuse through the pore. Currently, a model for eutectic solidification is not yet implemented in our numerical program and therefore the computation was stopped when Au concentration in the liquid pore/SL interface gap

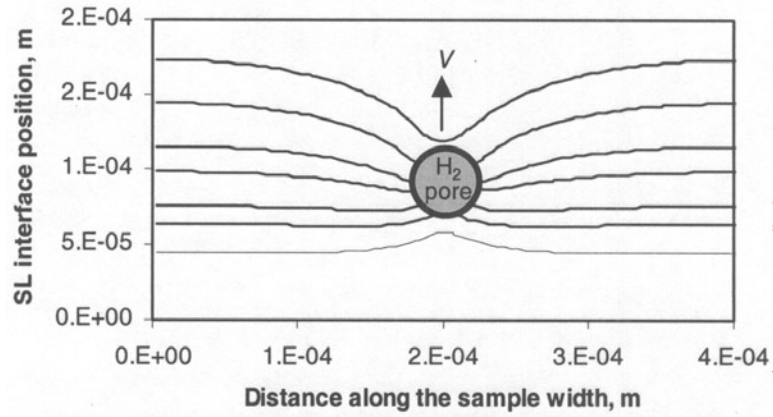


Fig. 7. Numerically calculated shape of the SL interface in various stages of engulfing a H_2 pore of fixed size (pure Al, $R_{pore} = 22.5 \mu m$, $V = 4 \mu m/s$, $G_L = 4.7 K/mm$)

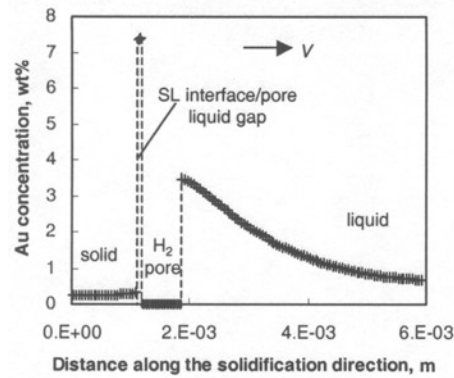


Fig. 8. Numerically calculated Au distribution profile along the sample centerline showing solute trapping in the SL interface/pore gap (Al-0.25 wt% Au, $V = 5 \mu m/s$, $G_L = 4.7 K/mm$)

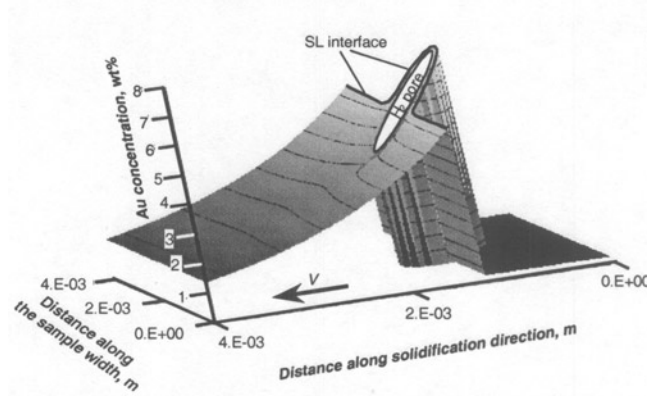


Fig. 9. Calculated Au concentration profile around a H_2 pore when the concentration in the pore/SL interface gap reaches the eutectic value (Al-0.25 wt% Au, $V = 5 \mu m/s$, $G_L = 4.7 K/mm$, $R_{pore} = 330 \mu m$) reached the eutectic value. This precluded a quantitative prediction of the second region of strong Au segregation developed in front of the pore after its complete engulfment.

Preparation for flight experiment

To obtain the necessary benchmark data for model validation, it is planned to have two sets of experiments on board the ISS. The first set consists of eight directional solidified samples in the quench module

insert (QMI) facility. This facility is a NASA-build module situated in the MSRR, Fig. 10. The sample-ampoule-cartridge-assembly (SACA) will contain the sample and the necessary instrumentation. It is planned to have two different designs available to perform directional solidification experiments with and without quench. The first set of experiments is designed to map the behavior of inert particles of different radii for pure metals and for solid-solution alloys. The second set will use the quenching capabilities of the QMI and is planned to capture the pushed particles at the solid/liquid interface of both pure matrices and alloy matrices, including the changes of the solutal field for the latter.

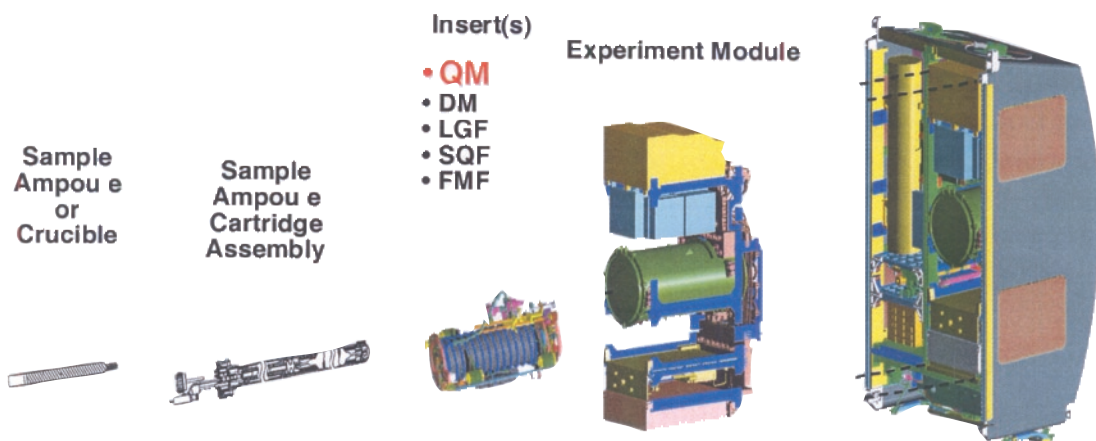


Fig. 10. Exploded view of the sample location within the Material Science Research Rack.

The material selection for the particles is zirconia of radii varying from 50 to 250 μm . The selection for the matrix materials is pure aluminum and zinc. To study the influence of the solutal field on the pushing-engulfment transition, solid-solution aluminum alloys were selected. An overview of the experiments planned for the first stage is given in Table 1.

The early flight opportunity provided by the LMS mission in 1996 enabled the testing of several experiment design options. Among these were the design of the ampoule, containing the liquid metallic sample and the subsequent task of free surface management. During the LMS mission, two designs were explored, one featuring a spring and piston design, while the other used an expansion void. The spring and piston design worked flawless in the $\mu\text{-g}$ environment and yielded a sound sample²². It is currently planned to use this design for the management of the free surface inside the ampoule. The drawback of this design is the requirement of tight tolerances between the ceramic piston and the ceramic ampoule to prevent any passage of the liquid metal and subsequent contact of the metal with the graphite spring. At the operating temperature, this would cause a reaction of the graphite with the aluminum metal and lead to the immobilization of the piston. Plans were developed for an alternative ampoule design where the spring is located in the cold zone. This requires for the ampoule to move within the cartridge and to have a perfectly sealed piston at the hot end, Fig. 11. This design, if successfully implemented, might provide an interesting solution to the challenges set forth by the spring and piston design.

Table 1. Matrix of the first set of PEP experiments to be processed without quench.

No.	Matrix	Particle		Solidification velocity, $\mu\text{m/s}$	Processed length, mm	Processing time, hrs
		type	radius, μm			
1	Al	ZrO ₂	50, 100, 250	0.3, 0.6, 1.2, 2.4, 4.8	125	44.82
2	Al	ZrO ₂	50, 100, 250	4.8, 10, 15, 20, 30	125	3.16
3	Zn	ZrO ₂	50, 100, 250	0.3, 0.6, 1.2, 2.4, 4.8	125	44.82
4	Zn	ZrO ₂	50, 100, 250	4.8, 10, 15, 20, 30	125	3.16
5	Al-Cu or Mg	ZrO ₂	50, 100, 250	0.1, 0.3, 0.6, 1.0, 1.5	125	99.5
6	Al-Cu or Mg	ZrO ₂	50, 100, 250	1.5, 2.0, 2.5, 3.2	135	17.32
7	Al-Ni eutect.	ZrO ₂	50, 100, 250	0.1, 0.3, 0.6, 1.0, 1.5	125	99.5
8	Al-Ni eutect.	ZrO ₂	50, 100, 250	1.5, 2.0, 2.5, 3.2	135	17.32

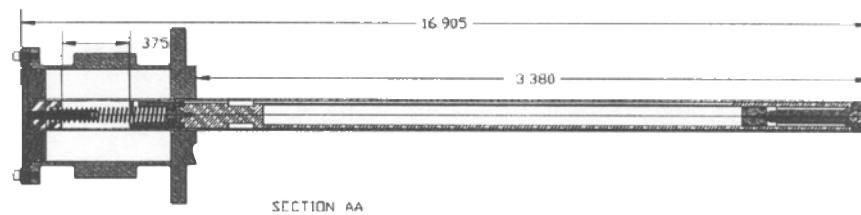


Fig. 11. Technical drawing of the alternative SACA concept with the spring located in the cold zone²³.

Other experimental design issues resolved by the experiments on LMS were the decision of the proper velocity profiles. It was found that a stepwise increase yielded better interface velocity control than a stepwise decrease. This is of importance when only a limited length of the sample can be used.

Based on the limitation of the experiment module (EM) and subsequently the QMI dimensions, the sample dimensions and further design criteria are given in Table 2. The quenching capabilities are based on a unique phase change device, which will be part of the SACA itself. This device features radially placed low melting point alloy blocks, which can be released onto the cartridge.

Table 2. Design criteria for the PEP experiment on board the ISS

Sample diameter	8 to 10 mm
Processing length	max. 200 mm, 150 mm with quench
Maximum processing temperature	900°C
Temperature gradient	<i>pure metals</i> 70°C/cm
	<i>alloys</i> 100°C/cm
Translation range	0.1 to 30 $\mu\text{m/s}$
Atmosphere	inert gas
Quench rate	ability to solidify within 2s with no melt-back of a 5mm axial section
Microgravity environment	10 ⁻⁴ g _o or less
Sample instrumentation	11 thermocouples

Contribution of the PEP project to Education and the Scientific Community

After its inception on the early 1990's, NASA has provided the PEP research effort with two shuttle experiments and the possibility of using the QMI on board the ISS. In reflection of NASA's agenda, the projects are expected to serve the furthering of scientific knowledge and the continuous education of future scientist. In light of these objectives, the PEP team has published 38 papers in journals and conference proceedings, the overwhelming majority of which are peer reviewed. An indicator of the scientific contribution of this research effort is the number of independent citations in refereed scientific journals, which, from 1990 to June 2001 were counted to be 247, Fig. 12. In addition, under the funding of this research effort nine (9) masters degrees were awarded, as were three (3) Ph.D. degrees.

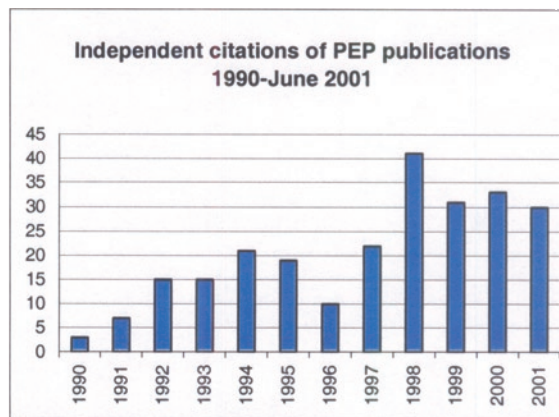


Fig. 12. Independent citations in refereed publications till June 2001

Acknowledgements

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CRYSTAL GROWTH OF ZNSE AND RELATED TERNARY COMPOUND SEMICONDUCTORS BY VAPOR TRANSPORT

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1. Introduction

The objective of the project is to determine the relative contributions of gravity-driven fluid flows to the compositional distribution, incorporation of impurities and defects, and deviation from stoichiometry observed in the crystals grown by vapor transport as results of buoyance-driven convection and growth interface fluctuations caused by irregular fluid-flows. ZnSe and related ternary compounds, such as ZnSeS and ZnSeTe, were grown by vapor transport technique with real time in-situ non-invasive monitoring techniques. The grown crystals were characterized extensively to correlate the grown crystal properties with the growth conditions.

2. Previous Accomplishments

The following is the research progress in the past two years. In-situ monitoring of partial pressure by optical absorption technique and visual observation of the growing crystal were performed during vapor growth of ZnSe [1]. Low-temperature photoluminescence (PL) spectra and glow discharge mass spectroscopy (GDMS) were measured on ZnSe starting materials provided by various vendors and on bulk crystals grown from these starting materials by physical vapor transport (PVT) to study the effects of purification and contamination during crystal growth process [2]. Optical characterization was performed on wafers sliced from the grown crystals of ZnSe, ZnTe and ZnSe_{1-x}Te_x (0<x<0.4). Energy band gaps at room temperature were determined from optical transmission measurements and a best fit curve to the band gap vs. composition, x, data gives a bowing parameter of 1.45 [3]. Low-temperature photoluminescence (PL) spectra of ZnSe and ZnTe were dominated by near band edge emissions and no deep donor-acceptor pairs were observed. The PL spectrum exhibited a broad emission for the ZnSe_{1-x}Te_x samples, 0.09<x<0.39. The single broad PL emission spectra and the spectra measured as a function of temperature were interpreted as being associated with the exciton bound to Te clusters because of the high Te content in these samples [3].

3. Recent Results

a) Beer Law constants and vapor pressures of HgI₂ over HgI₂(s,l)

To validate numerical codes, in-situ monitoring during the PVT of HgI₂ was designed. The α-HgI₂ starting material was vacuum sublimated four times before zone refining in a zone refiner that produced a 1-in. melting zone. Fused silica tubing of 13 mm O. D., 10 mm I. D., and 60 cm in length was used as the zone-refining ampoule. The ampoule was first cleaned with an acetic-nitric-hydrofluoric acid solution, rinsed with de-ionized water and out-gassed under 10⁻³ Torr vacuum for 2 h. Then α-HgI₂ starting materials with a typical weight of about 100 g were loaded into ampoules. A total of 100 vertical zone passes with a zone travel rate of 8.5 cm/h were used. After the completion of the zone-refining process, the ampoules were

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opened to recover the refined materials. The sample from the middle section (purest) was extracted and ground into powder.

The T-shaped optical cells were made of fused silica. The top of the T-shaped cell consisted of a 18 mm O.D., 15 mm I.D., cylindrical tube with flat, parallel windows and an optical path of about 10 cm. The bottom of the T-cell was a sidearm attached to the midpoint of the cell-proper. Two cells were made; HgI₂-1 was used to measure the optical absorption of HgI₂ sample as a function of temperatures and the other cell, HgI₂-2, was designed to measure Beer's Law constants by completely vaporizing the sample inside. For the HgI₂-1 cell, the sidearm was made by joining a 6 cm long, 12 mm O.D., 8 mm I.D. tube and a 10 cm long 18 mm O.D., 15 mm I.D. tube coaxially. The sidearm for the HgI₂-2 cell was made by joining a 2.5 cm long, 12 mm O.D., 8 mm I.D. tube and a 20 cm long 32 mm O. D., 28 mm I.D. tube. The 12 mm O.D. part was attached to the cell-proper and referred to as the stem and the larger O.D. part of the sidearm is referred as the reservoir section. For both cells, a 12 mm O. D., 8 mm I.D. tube was attached to the reservoir section for vacuum connection during seal-off. The volumes of the empty cells were measured as a function of the length along the sidearm by adding distilled water with 0.1 ml resolution. The empty cells were successively rinsed with distilled H₂O, 49 wt. % HF, distilled H₂O, methanol, distilled H₂O, acetone, and distilled H₂O and then dried in a box furnace at about 130°C. The cells were baked at about 850°C for 18 h under vacuum.

For the HgI₂-1 cell, 4.5765 g sample was weighed out using a Mettler AT 201 balance and loaded directly into the baked-out ampoule. For the complete vaporization cell, HgI₂-2, two small specks of HgI₂ were first loaded into a cleaned and baked quartz well (6 mm O. D., 4 mm I. D. and 2 cm long) to prevent any sample loss from sticking to the tubing wall during loading. The sample weighed 12.128 mg as determined with a Chyo Jupiter M1-20 microbalance, which was calibrated to an accuracy tolerance of 0.005 mg. The well was then slid into the optical proper region of the HgI₂-2 cell to minimize the loss from vaporization during seal-off. Both cells were sealed off at 1×10^{-4} Torr vacuum after 30 min of evacuation. The free volume of the cells were then determined from the sealed positions and were 36.2 ml and 138.0 ml, respectively, for HgI₂-1 and -2.

The sealed cells were placed in a five-zone T-shaped furnace. The top of the T was approximately 30 cm long and 4 cm I.D. and had three independently controlled heating zones. The two zones on the side (zone 1 and 3) consisted of two 7.5 cm long semi-cylindrical heating elements connected in parallel, and the central zone (zone 2) had one 7.5 cm long semi-cylindrical element. A ceramic tube liner, 28 cm long, (not shown in Figure 1) is positioned between the furnace bore and the optical cell-proper to block any stray light. The stem and the reservoir sections were heated, respectively, by a 4 cm I.D., 7.5 cm long and a 6.5 cm I.D., 30 cm long cylindrical element. A 45 cm long, 4 cm I.D., 6 cm O.D. heat pipe furnace liner (Dynatherm Corp.), with Hg working fluid inside, was inserted between the furnace bore and cell reservoir section to improve sample isothermality. Three K-type thermocouples, calibrated with standards and instrumentation traceable to N.I.S.T, were positioned along the optical cell-proper and three more along the stem and the sample section to check the temperature uniformity along the sample.

The furnace with the optical cell inside was then placed in the path of the sample beam of a double-beam, reversed-optics spectrophotometer (OLIS Inc., model 14H) with the reference beam passed under the furnace. The optical density, defined as $D = \log_{10}(I_{\text{reference}}/I_{\text{sample}})$, where I is the intensity (of reference or sample beams), was measured between the wavelength of 200 and 600 nm. The light source was a

deuterium lamp for wavelengths below 288 nm and a Xenon lamp for wavelengths above 288 nm. The typical instrument band pass was 0.16, 1.1, and 2.7 nm, respectively at the wavelengths of 600, 288, and 200 nm. The temperature of the optical cell-proper, $T_{o.c.}$, was kept at 230, 260, 300 or $340 \pm 1^\circ\text{C}$, while the stem and the reservoir sections were maintained at a temperature that was the same as or lower than $T_{o.c.}$. A baseline spectrum was measured first for each $T_{o.c.}$ with the reservoir temperature below 50°C .

For the HgI_2 -1 cell, the optical density was measured with $T_{o.c.}$ at either 230 or 340°C , while the reservoir maintaining at a temperature lower than $T_{o.c.}$. A series of spectra were then measured for increasing reservoir/sample temperatures with times at fixed sample temperature generally about 20 min. For the HgI_2 -2 cell, the $T_{o.c.}$ was initially set at 230°C and the optical density was measured as reservoir temperature increased. Between the reservoir temperature at 188 and 210°C , the measured optical density at specific wavelengths stopped to increase as temperature increased - indicating a complete vaporization of the sample. Then, the optical density spectra were measured with the whole cell under isothermal condition at 230, 260, 300, and 340°C to establish the Beer's Law constants.

The measured optical density for the HgI_2 -1 cell, plotted in Figure 1, shows a triple-peak spectrum between 200 and 400 nm wavelength region. Neither the atomic absorption for the $\text{Hg } 6^1\text{S}_0 - 6^3\text{P}_1$ transition at 254 nm nor the vibronic absorption spectrum for I_2 molecule from 400 to 600 nm with a maximum at 505 nm were observed. The measured spectrum is consistent with the published absorption spectra for HgI_2 [9]. Since there was no absorption observed at the wavelength of 600 nm, the net optical density was obtained by subtracting the baseline from the measured spectrum with a correction of the baseline shift determined from the measured optical density at 600 nm. The measurable upper limit for D was 3.5 to 4, where the sample beam intensity reduced to the same order of magnitude as the dark current in the photomultiplier tube. The net optical density, D , for a set of wavelengths between 200 and 440 nm were plotted against $1000/T$, where T is the reservoir temperature in K. For both $T_{o.c.}$ (230 and 340°C), the data for each wavelength are parallel, implying that the absorption in the range of these wavelength was from the same vapor species. For the HgI_2 -2 cell, the plot of D vs. $1000/T$ clearly shows that the sample completely vaporized at $197 \pm 1^\circ\text{C}$. The errors in the measured D and temperatures were estimated to be less than ± 0.001 , and $\pm 1.0^\circ\text{C}$, respectively.

In the subsequent isothermal runs for the HgI_2 -2 cell, the measured D were off-scale for all the wavelengths below 300 nm, except at 212 nm, and were too low to be reliable for wavelengths higher than 400 nm. The measured D for six wavelengths, i.e. 212 nm and 5 wavelengths between 300 to 380 nm, were used to determine Beer's Law constants, α . The pressure was calculated from ideal gas law, $P = nRT/V$, where n , R and V are, respectively, the number of mole, gas constant and the free volume. Table 1 gives the Beer's Law constants of HgI_2 species for these 6 wavelengths at four different temperatures, 230, 260, 300, and 340°C .

Using the Beer's Law constants given in Table 1, the vapor pressures of HgI_2 as a function of temperatures were determined from the measured D in the HgI_2 -1 runs. The pressure value was taken as the average of, typically, 4 to 6 wavelengths and is plotted as a function of $1000/T$ in Figure 2. The measured pressures ranged from 9×10^{-6} to 0.8 atm and the results from the optical cell temperatures at 340 and 230°C agree well. The data measured by Abraham et al. [4] in the temperature range of 417 and 509 K is given as the dotted line. Our data agree well with their data in the temperature range of 417 to 460 K and are a little higher in the high temperature region. The HgI_2 pressures measured by Piechotka et al. [5] were

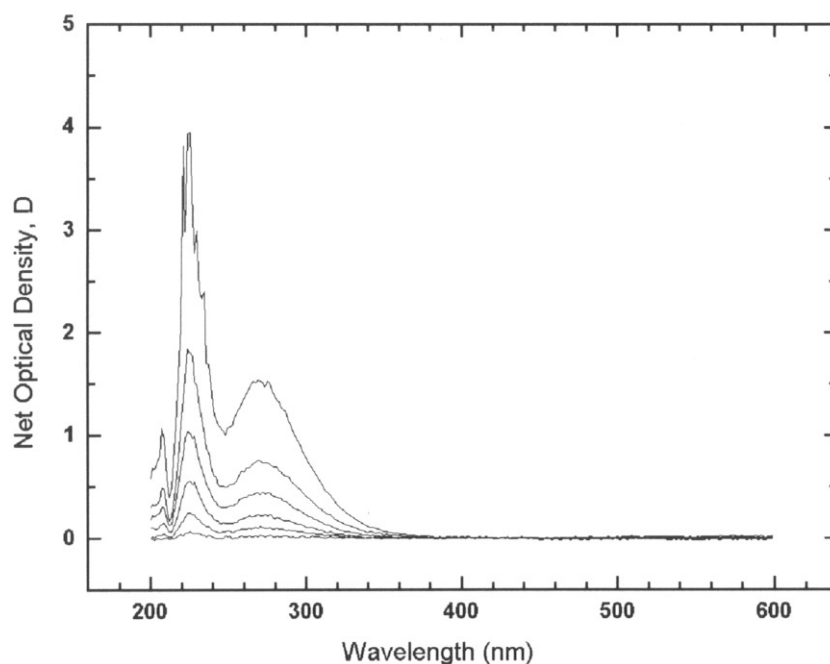


Figure 1. Optical absorption spectra of HgI_2 vapor species at six different reservoir temperatures from low to high absorption as 360, 386, 408.4, 419.8, 429.6, and 443.9K. ($T_{\text{o.c.}} = 340^\circ\text{C}$)

Table 1. Beer's Law constants, α , in atm-cm for HgI_2 vapor species.

Wavelength (nm)	α at 230 °C	α at 260 °C	α at 300 °C	α at 340 °C
212	0.0851	0.0831	0.0833	0.0799
300	0.0335	0.0352	0.0359	0.0379
320	0.0914	0.0894	0.0861	0.0855
342	0.3377	0.3101	0.2849	0.2739
360	1.0637	0.9739	0.8398	0.7420
380	3.6759	3.9883	2.7200	2.6388
208	0.0201*			0.0260*
224	0.00658*			0.00759*
230	0.00912*			0.00938*
242.5	0.0276*			0.0262*
265	0.0148*			0.0188*
280	0.0169*			0.0214*
400	2.1435*			7.6955*
420	4.0307*			23.680*
440	4.4392*			79.119*

* α determined from HgI_2 -1 runs

represented by three expressions for temperatures between 300 and 420 K. The expressions for the two high temperature sections are shown as the dashed line in Figure 4. In general, the agreement between our 600

data and their results are good. Omalý et al. [6] claimed to deduce from the JANAF thermodynamic data [7] the HgI_2 equilibrium pressures, which is shown as the lowest dashed-dotted line.

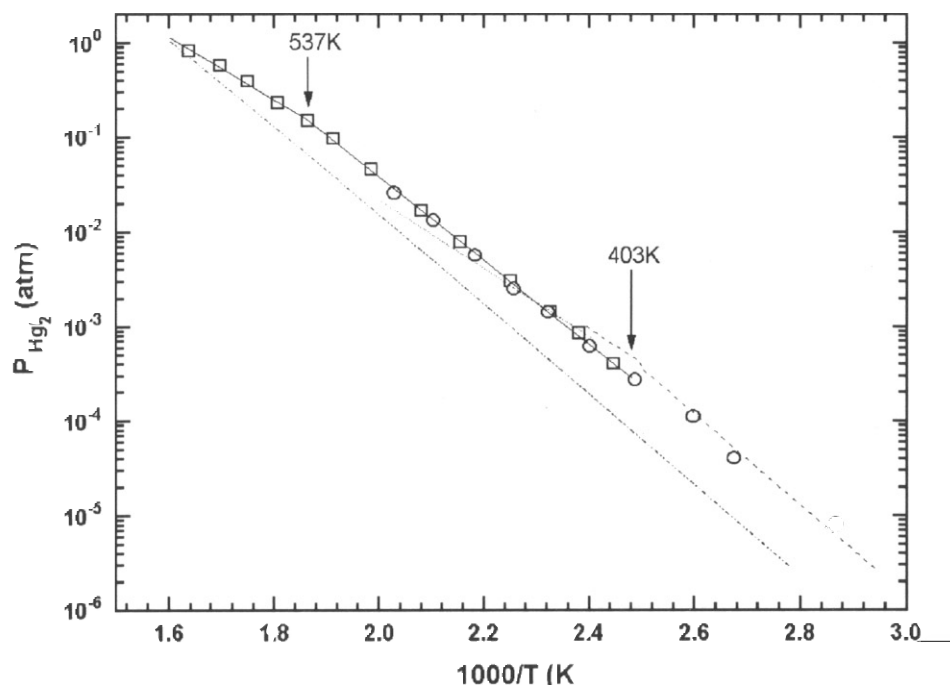


Figure 2. $\log_{10} P_{\text{HgI}_2}$ vs. $1000/T$, where T is reservoir temperature in K. Squares and circles are measured for $T_{\text{o.c.}}$ at 340 and 230°C, respectively. The two solid line segments are given by Eq. (1) and (2). The dashed line at low temperature region is from Ref. [5], and the dotted line in the middle temperature range is from Ref [4]. The lowest dashed-dotted line is from Ref [6].

The temperature for the α to β - HgI_2 transition as well as the melting point were studied by Differential Scanning Calorimetry [8] and were found to be dependent on the purity and stoichiometry of the sample. For the high purity sample, the α to β transition and the melting point were found to be 405 ± 2 K and 531 ± 1 K, respectively. Therefore, the vapor pressure data for $T > 531$ K and $405 < T < 531$ K were fit linearly on the $\ln P$ vs. $1/T$ plot and the best fits are as follows:

$$\ln P (\text{atm}) = -7,700/T + 12.462 \quad T > 531 \text{ K} \quad (1)$$

$$\ln P (\text{atm}) = -10,150/T + 17.026 \quad 405 < T < 531 \text{ K} \quad (2)$$

The expressions correspond to the enthalpies of vaporization and sublimation of 15.30 and 20.17 Kcal/mole, respectively, for the liquid and the β -phase HgI_2 , and the intersection of the two expressions gives a melting point of 537 K. The difference in the enthalpies gives an enthalpy of fusion of 4.87 Kcal/mole. The enthalpy of sublimation for β - HgI_2 , 20.17 Kcal/mole, is in good agreement with previous results of 20.267 Kcal/mole [5] and 20.0 Kcal/mole [9] and is about 2 % higher than the value of 19.789 Kcal/mole given in Ref. [4]. The enthalpy of fusion agrees well with the value of 4.9 Kcal/mole [9] and about 8 % higher than the value of 4.5 Kcal/mole quoted in Ref. [7] and [10].

The Beer's Law constants for those wavelengths other than listed in Table 1 can be calculated from the P_{HgI_2} for each of the HgI_2 -1 runs, the measured D for the specific wavelength, and the path length. The Beer's Law constants were then taken as the average of the calculated values from 4 to 6 runs at different

reservoir temperatures. Table 1 lists the Beer's Law constants for these wavelengths at the specific optical cell temperature, 230 or 340°C. Using these Beer's Law constants and the measured D, one can calculate the pressures for each of the HgI₂-1 runs and, as expected, they agree well with the data presented in Figure 4 except that a value for P_{HgI₂} at the lowest reservoir temperature, 349K, was obtained.

The extinction coefficients at 342 nm were determined [4] as a linear function of T:

$$\epsilon \text{ (liter mole}^{-1} \text{ cm}^{-1}\text{)} = 0.803 T \text{ (K)} - 273.1 \quad (3)$$

The Beer's Law constants, α , can be converted to the extinction coefficient using $\epsilon = RT/\alpha$. The values for ϵ at 342 nm calculated from the values for α given in Table 1 were 122.237, 141.076, 165.065, and 183.711, respectively, for 230, 260, 300, and 340 °C. The values given by Eq. (3) are 7, 10, 13, and 19 % higher than our data at 260, 260, 300, and 340°C, respectively.

There were three P_{HgI₂} data below 405 K for the solid α -phase, and they show a similar slope in the log P vs. 1/T plot as that for the β -phase. The enthalpy of sublimation for α -HgI₂ was not determined because there were not enough data points and also because, in the 10⁻⁶ to 10⁻⁴atm range, the associated errors in the measured P were relatively large. Since the reported enthalpy of transition from α to β -HgI₂ was small, about 640 cal/mole [10], the slope of the log P vs. 1/T plot for the α -phase should be very close to that for the β -phase. The enthalpy of vaporization for the liquid phase was determined from five data points and, therefore, the error was larger than the enthalpy of sublimation for the β -phase, which was determined from 15 data points. Consequently, the heat of fusion and the melting point, which were derived from the two expressions in Eq. (1) and (2), will inherit the error for the liquid phase. However, it should be noted that the errors associated with the Beer's Law constants only affect the absolute values of the measured pressures, but not the slope in the log P vs. 1/T plot.

b) Partial Pressures for Several In-Se Compositions from Optical Absorbance of the Vapor

The optical absorbance of the vapor phase over various In-Se compositions between 33.3 and 60.99 at% and 673 to 1418 K has been measured and used to obtain the partial pressures of Se₂(g) and In₂Se(g) [11]. The results are in agreement with silica Bourdon gage measurements for compositions between 50 and 61 atomic % but significantly higher than those from Knudsen cell and simultaneous Torsion-Knudsen cell measurements. It is found that 60.99 at% Se lies outside the sesquiselenide homogeneity range and 59.98 at% Se lies inside and is the congruently melting composition. The Gibbs energy of formation of the liquid from its pure liquid elements between 1000 and 1300 K is essentially independent of temperature and falls between -36 and -38 kJ per gram atomic weight for 50 and 56 % Se at 1200 and 1300 K.

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STRUCTURAL FLUCTUATIONS AND THERMOPHYSICAL PROPERTIES OF MOLTEN II-VI COMPOUNDS

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The objectives of the project are to conduct ground-based experimental and theoretical research on the structural fluctuations and thermophysical properties of molten II-VI compounds to enhance the basic understanding of the existing flight experiments in microgravity materials science programs as well as to study the fundamental heterophase fluctuation phenomena in these melts by:

- 1) conducting neutron scattering analysis and measuring quantitatively the relevant thermophysical properties of the II-VI melts (such as viscosity, electrical conductivity, thermal diffusivity and density) as well as the relaxation characteristics of these properties to advance the understanding of the structural properties and the relaxation phenomena in these melts and
- 2) performing theoretical analyses on the melt systems to interpret the experimental results.

All the facilities required for the experimental measurements have been procured, installed and tested. It has long been recognized that liquid Te presents a unique case having properties between those of metals and semiconductors. The electrical conductivity for Te melt increases rapidly at melting point, indicating a semiconductor-metal transition. Te melts comprise two features, which are usually considered to be incompatible with each other: covalently bound atoms and metallic-like behavior. ‘Why do Te liquids show metallic behavior?’ is one of the long-standing issues in liquid metal physics. Since thermophysical properties are very sensitive to the structural variations of a melt, we have conducted extensive thermophysical measurements on Te melt.

The Torsion Oscillation Cup Method

The torsion oscillation cup method, which was employed at MSFC to measure the viscosity of HgTe, HgCdTe and HgZnTe melts is a practical method for a nonintrusive measurement of the viscosity of melts at high temperatures and under high pressures [1, 2]. The method involves the measurements of the damped oscillatory motion of a vertical cylindrical crucible containing the melt attached by means of a torsion wire. The disadvantage of the technique is that the measurement time is too long, one to two hours, to study the dynamics of phase transformations, or homogenization processes with characteristic times on the order of minutes. Sometimes it is also difficult to maintain stable test condition, especially at high temperatures. A number of factors, including drift in the physical properties of torsion wire over long time periods at elevated temperatures, can influence the precision of the method. Recently, through the NASA Advanced Technology Development (ATD) program, we have developed a novel technique to nonintrusively and simultaneously measure viscosity and electrical conductivity of metallic and semiconductor melts. The essential feature of this technique is the utilization of an axial rotating magnetic

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field (RMF), as shown in Figure 4, which induces controllable fluid flows in the melt. The RMF causes a rotation of the fluid that in turn exerts a torque on the wall of the stationary enclosure. When the force inducing the fluid motion is removed, the rotation of the fluid decays and the fluid comes to rest. The characteristics of the transient torque decay can be used to calculate the fluid viscosity and the steady-state torque applied to the enclosure by a given magnetic field to calculate the melt electrical conductivity.

The rotating motion of the ampoule is measured by the angular deflection of the quartz fiber (torsion wire) as a function of time using an optical encoder (Micro-E, Inc.). An evacuated bell jar is being used to reduce noise caused by air currents and allows more reproducible and precise measurements of the angular deflection. A typical result for a HgTe sample is given in Figure 6, where the measured deflection angle is shown as a function of time. The RMF was turned on at time about 40s, then turned off at about 230s, and the ampoule was then free to rotate. Two methods were developed to analyze the data. The first one is an analytical method. The stationary torque caused by the applied RMF can be determined from the average of the deflecting angular oscillations. The electrical conductivity can be derived by comparing the torque with that of a standard sample of known electrical conductivity, such as Hg or Ga melt, sealed inside an ampoule of identical dimensions. The measured angular deflection after the RMF has been turned off is similar to that of an oscillation-cup viscometer and its logarithmic decrement can be utilized to determine the viscosity analytically by the approximate Roscoe formula [2, 3].

In the second method, the coupled equations for fluid flow and ampoule torsional vibrations were solved numerically [4]. The unknown variables, electrical conductivity and viscosity of the melt, were allowed to vary to obtain a best fit to the experimental data of deflecting angle vs. time. As seen in Figure 6, the simulation results are in a good agreement with the experimental data; the ratio difference between the experimental and calculated results is less than 10^{-4} . The transient velocity of the melt caused by the rotating magnetic field was found to reach equilibrium in about half a minute and the viscosity of melt could be determined from the magnitude of the oscillation. This allows a viscosity measurement in a minute or so, in contrast to the existing oscillation cup method, which requires at least an hour for a measurement. We have also performed measurements under identical conditions except for the various RMF running times (1 to 15 min) that were used to take the data. The numerical analysis yielded nearly identical values as those determined analytically for the electrical conductivity and viscosity. For example, the best fit, shown in Figure 6, gives a value of $3.04 \times 10^{-7} (\text{m}^2/\text{s})$ for Te melt at 470°C compared to the value of $3.1 \times 10^{-7} (\text{m}^2/\text{s})$ determined by an approximate analytical method.

The viscosity can be obtained by numerically solving the melt flow and ampoule oscillation equations simultaneously with viscosity as the adjustable parameter and fitting the solution to experimental deflection-time data. The ampoule rotational oscillation can be described as:

$$I\omega^2 \left[\frac{d^2\alpha(t)}{dt^2} + 2\Delta_0 \frac{d\alpha(t)}{dt} + (1 + \Delta_0^2)\alpha(t) \right] = M(t)$$

where the ampoule-melt interaction (torque exerted by melt flow on ampoule wall) is:

$$M(t) = -2\pi R^2 h \rho v \left. \frac{dV_\theta}{dr} \right|_{r=R}$$

The melt rotational flow under RMF is:

$$\frac{\partial V_\theta}{\partial t} = f_\theta + v \left(\frac{\partial^2 V_\theta}{\partial r^2} + \frac{1}{r} \frac{\partial V_\theta}{\partial r} - \frac{V_\theta}{r^2} \right)$$

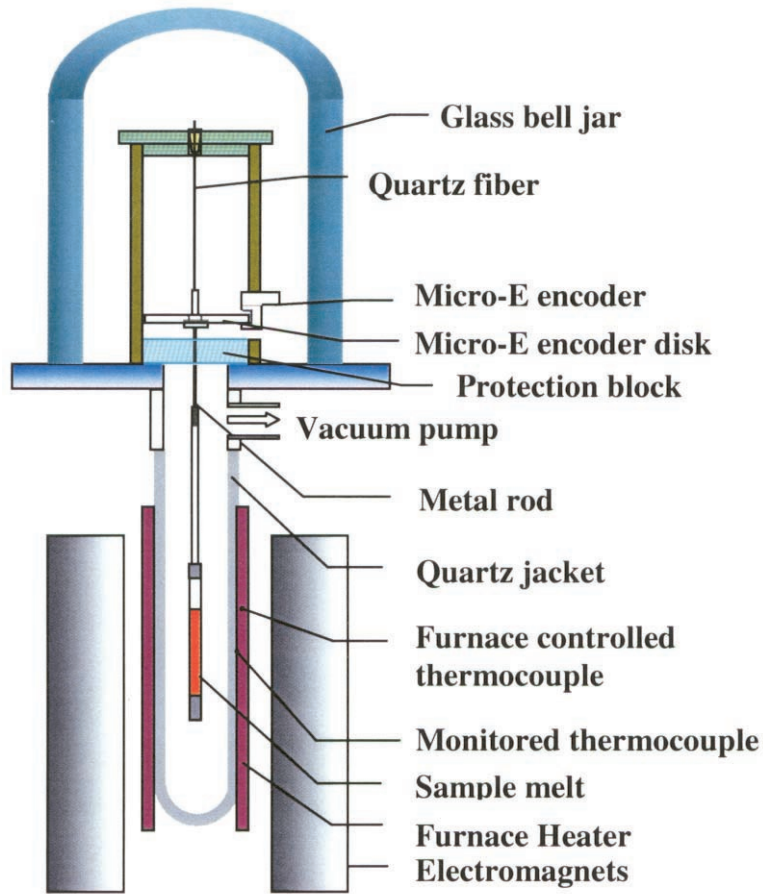


Figure 1. Schematics of the viscometer with the rotating magnetic field.

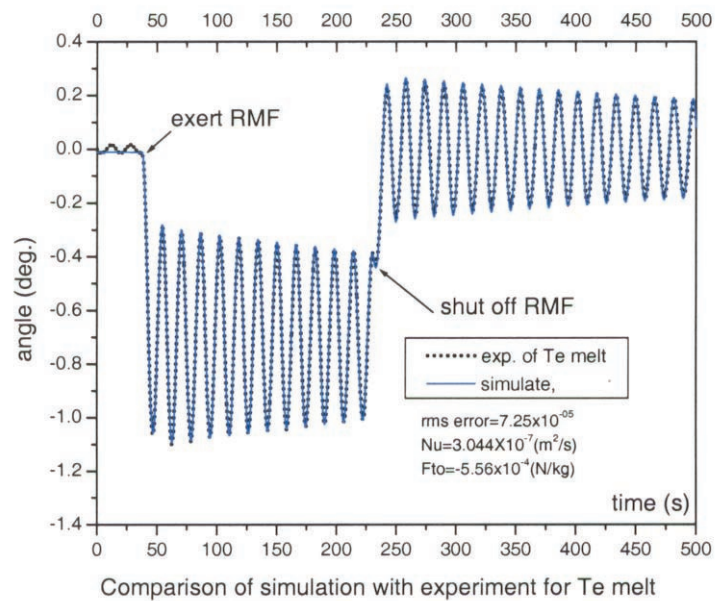


Figure 2. The angular deflection vs. time for HgTe melt. The dotted line is the experimental results and the blue solid line the calculated results

Where the Lorentz force f_g is given by:

$$f_{\theta} = f_{\theta 0} \cdot \frac{r}{R\omega_o} \left(\omega_o - \frac{V_{\theta}}{r} \right)$$

and the initial and boundary conditions are:

$$V_{\theta}(r,t)=0, \text{ when } t=0; \text{ and } V_{\theta}(R,t)=R \frac{d}{dt}$$

The electrical conductivity of the melt can be determined from the torque induced by the melt flow at equilibrium:

$$M_{eq} = \frac{\pi}{4} B_0 \sigma \omega h R^4$$

NOMENCLATURE

B_0	magnetic induction	α	deflection angle of the ampoule
f_g	Lorentz force	V_{θ}	fluid rotational velocity
h	height of the melt in the ampoule	σ	electrical conductivity of the melt
I	moment of inertia of system	ω_0	angular velocity of RMF
M	torque induced by melt flow	ρ	density of the melt
R	radius of the ampoule	Δ_0	logarithmic decrement of oscillation
t	time	ν	kinematic viscosity of the melt
r	radial coordinate		

The measured kinematic viscosity of Te melt as a function of temperature as shown in Figure 3. Comparing with the previous results [5] our data are generally low by about 10%. However, the most prominent feature of our data, which was not reported before, is the sharp peak of viscosity, which was reproducibly observed in the temperature range between 500 and 560°C. The measured electrical conductivity of Te melt is given in Figure 4. Our data agree well with previous results and confirm the semiconducting-metallic transition just above the melting point.

Thermal diffusivity and heat capacity.

A dynamic measurement of thermal diffusivity using the laser flash method [6, 7] has been employed previously to determine the thermal conductivity of various composite materials as well as materials that have to be enclosed in closed ampoules due to their high vapor pressures or toxic nature. In this method, the front surface of a small disk-shaped sample positioned vertically inside a furnace is subjected to a very short burst of radiant energy from a laser pulse with a radiation time of 1ms or less. The resulting temperature rise of the rear surface of the sample is measured and thermal diffusivity calculated from the temperature rise versus time. The thermal diffusivities of $Hg_{1-x}Cd_xTe$ solids and melts [8], pure Te, Te-rich HgCdTe and Te-rich HgZnTe melts [9] were determined using this technique. Using the technique we have also measured the thermal diffusivities for $Hg_{1-x}Zn_xTe$ solids and melts [10].

During this project, we have constructed the instrumental setup for thermal diffusivity measurements as schematically shown in figure 5. A pulsed laser beam with 1064 nm wavelength was focused to 10 mm diameter and to illuminate one side of the Te melt. The laser energy variation from pulse to pulse at defined energy was 1% and the pulse duration used in experiments was 1 millisecond. An inferred CdZnTe

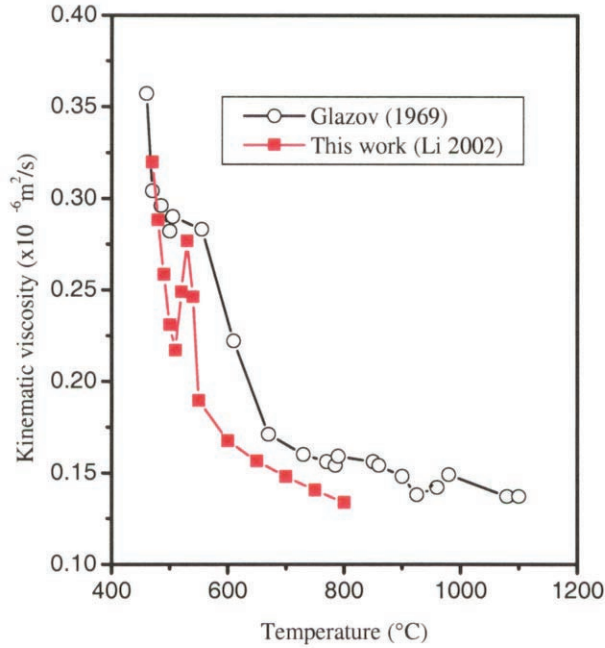


Figure 3. Measured kinematic viscosity of Te melt as a function of temperature.

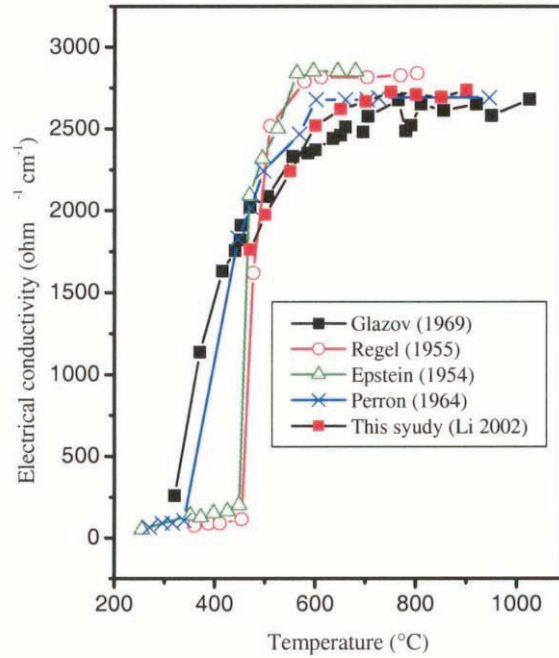


Figure 4. Measured electrical conductivity of Te melt as a function of temperature.

detector was installed at the other side of the sample cell and was focused at the sample center with a 2 mm diameter spot. The detector ranges from 723 K to 1473 K.

We can simultaneously determine the specific heat and thermal diffusivity of a sample by performing numerical simulation of overall heat transfer. Very well defined boundary conditions are required to match the experimental and simulation conditions. We are using a YAG laser for the radiation source, with a 608

spatially uniform intensity as close as possible to a delta function, and the beam diameter at the front surface of the sample cell can be adjusted to match the sample diameter.

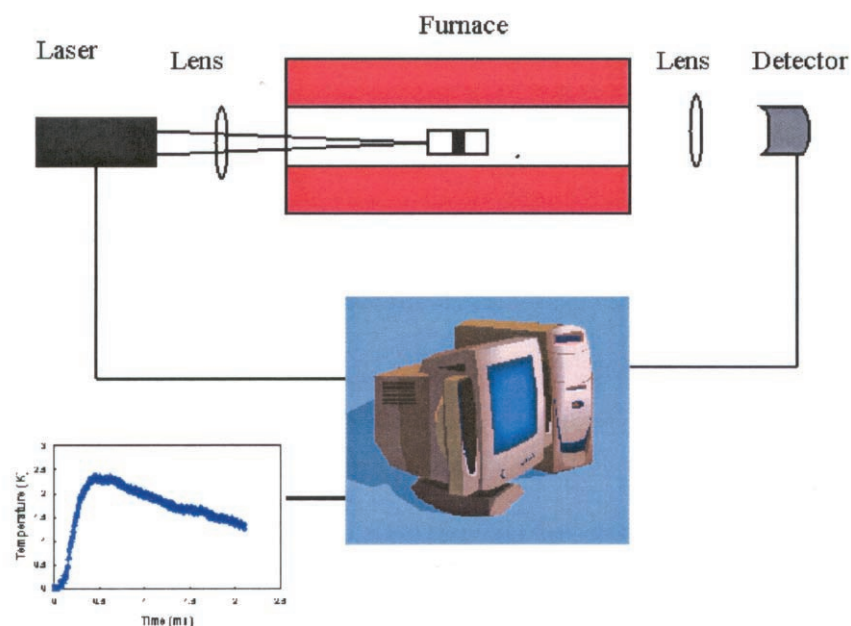


Figure 5. The schematic apparatus of laser flash measurement

Te powder was sealed in a specially designed cylindrical-shape optical quartz cell. The outer and inner diameters of the optical cell are 15 mm and 10 mm, respectively. The cell was 22 mm long and the sample thickness was about 2 mm. Sample was clamped into a stainless steel block that is placed at the center of a furnace with a heat pipe made of stainless steel. The temperature-uniform zone was about 10 cm and the variation in the measurement range was less than 0.5 K. Before making the measurements, the cell containing Te powder was first heated at 1083 K for 48 hours to ensure the Te was in a homogeneous liquid state. After reaching the steady state at measurement temperature, five thermal diffusivity measurements were performed at this temperature. Between each measurement, a 15-minute waiting period was used to let the liquid T back to same initial state. Sample was measured when it was heated up and cooled down. The radiation energy was collected and converted into temperature at 1 KHz rate. The measurement started about one second before the laser illumination and last for 10 seconds. Figure 6 shows first two-second part of a thermal diffusivity transient of Te melts at 873 K.

The specific heat of Te melt deduced from the numerical fit in the measuring temperature range is shown in figure 7. As a comparison, several curves originated from published references [11-13] are also plotted in the figure.

The thermal diffusivity data, which is shown in figure 8, are calculated from the experimental data by using an analytic method. Measurements from both rising and cooling temperature processes are plotted in this figure. The data are almost overlapped within the error range. The variation of each data point is about 3%. Thermal diffusivity data measured by Maleki and Holland [9] are also plotted in the figure 4, which agrees well with our data at low temperatures. Their measurements stopped at 923 K without any indication of the temperature-dependent at high temperatures. Our experiment data show that a similar

linear temperature-dependent of thermal diffusivity extended to 1023 K. After this temperature, however, the thermal diffusivity keeps at a nearly constant value.

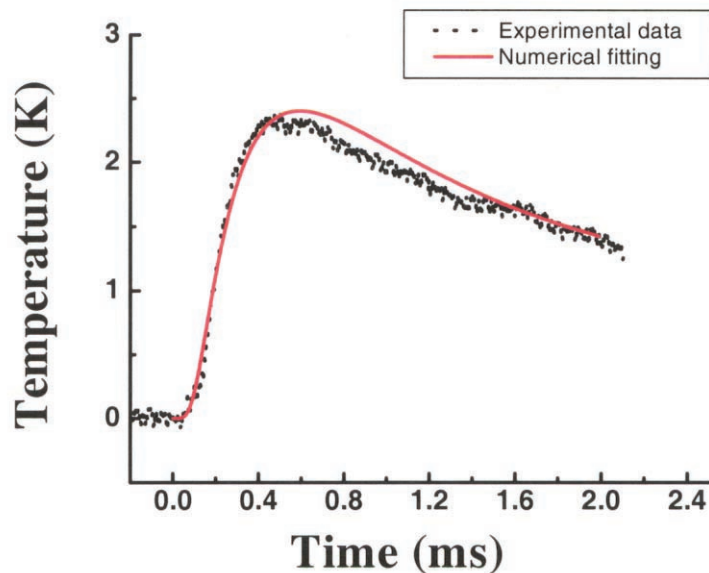


Figure 6. Temperature transient curves of liquid Te at 873 K, (dot line) experimental measurement and (solid line) numerical fitting.

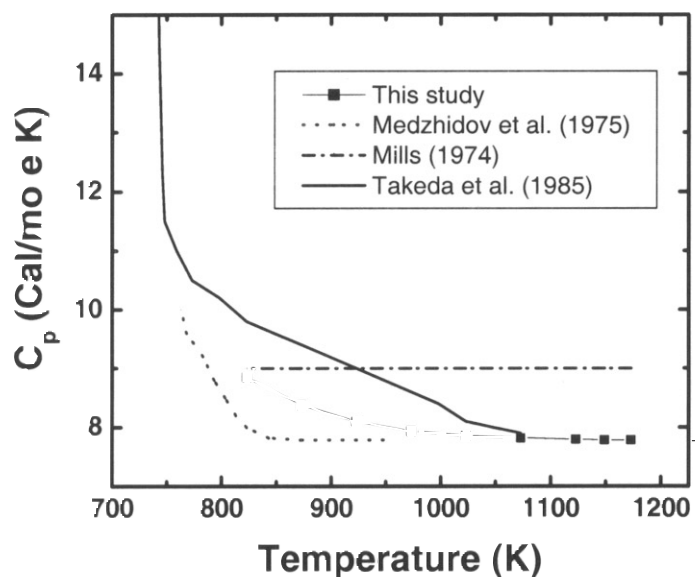


Figure 7. Specific heat curve of liquid Te as a function of temperature.

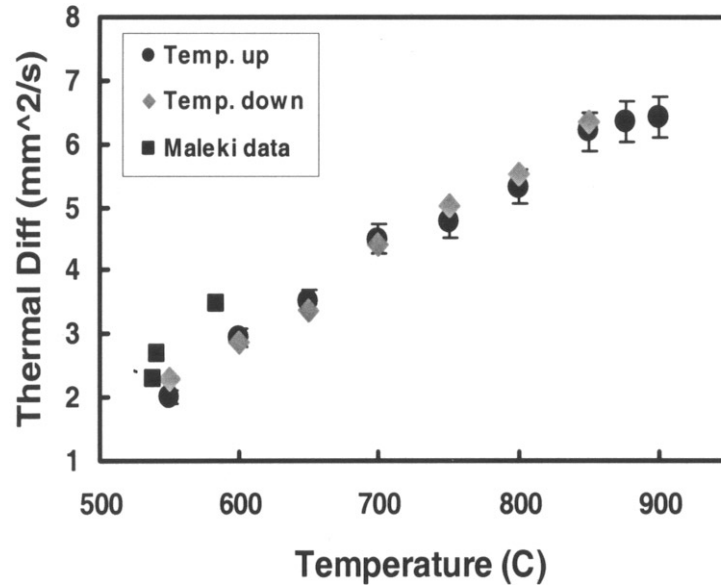


Figure 8. Thermal diffusivity vs. temperature for liquid Te

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REDUCTION OF DEFECTS IN GERMANIUM-SILICON

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Objectives of the Investigation

Crystals grown without being in contact with a container have superior quality to otherwise similar crystals grown in direct contact with a container, especially with respect to impurity incorporation, formation of dislocations, and residual stress in the crystals. In addition to float-zone processing, detached Bridgman growth, although not a completely crucible-free method, is a promising tool to improve crystal quality. It does not suffer from the size limitations of float zoning and the impact of thermocapillary convection on heat and mass transport is expected to be negligible. Detached growth has been observed frequently during μg experiments [1]. Considerable improvements in crystalline quality have been reported for these cases [2]. However, neither a thorough understanding of the process nor a quantitative assessment of the quality of these improvements exists. This project will determine the means to reproducibly grow GeSi alloys in a detached mode and seeks to compare processing-induced defects in Bridgman, detached-Bridgman, and floating-zone growth configurations in GeSi crystals ($\text{Si} \leq 10 \text{ at\%}$) up to 20mm in diameter.

Specific objectives include:

- measurement of the relevant material parameters such as contact angle, growth angle, surface tension, and wetting behavior of the GeSi-melt on potential crucible materials;
- determination of the mechanism of detached growth including the role of convection;
- quantitative determination of the differences in defects and impurities for crystals grown using normal Bridgman, detached Bridgman, and floating zone (FZ) methods;
- investigation of the influence of a defined flow imposed by a rotating magnetic field on the characteristics of detached growth;
- control of time-dependent Marangoni convection in the case of FZ growth by the use of a rotating magnetic field to examine the influence on the curvature of the solid-liquid interface and the heat and mass transport; and
- growth of benchmark quality GeSi-single crystals.

Microgravity Relevance

Prior to the beginning of this investigation, the most reliable environment for obtaining detached Bridgman growth was reduced gravity. At this time, we and others are repeatedly growing partially detached Bridgman samples in unit gravity. Nonetheless, the reasons for completing the microgravity parts of this investigation still remain viable:

Keywords: detached Bridgman growth, crystal growth, germanium, germanium-silicon

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- The comparison of samples grown by detached growth with float-zone samples of the same diameter is fundamental to this study because the float-zone technique is truly and completely containerless in contrast to detached Bridgman growth. Terrestrial floating zones of this material are limited to diameters of about 8mm. Therefore, these larger diameter floating-zone experiments can only be conducted in a reduced gravity environment.
- The occurrence of detachment during Bridgman growth is postulated to be dependent upon the difference in gas pressures in the crucible above and below the melt and it is further believed that the evolution of gases at the growth interface is required to maintain the necessary pressure difference [3, 4, 5]. Determining whether this pressure difference is essential in all cases is one of the objectives of this investigation. If the growth and contact angles are favorable, detachment will take place without a pressure difference. This will only be possible for very few material-crucible combinations. Gas evolution and the resulting maintenance of the pressure difference will be strongly effected by convection in the melt, which is dominated in the Bridgman configuration by buoyancy-driven flows. Thus, to the extent that this phenomenon is necessary for detachment, the conditions for detached growth will differ significantly between unit gravity and microgravity because of the influence of gravity on convection in the melt.
- The effect of an intentional pressurization of the volume below the meniscus either by using pressurized gas [6] or by changing the temperature profile, as in this project, is limited by the emission of bubbles under gravity once the pressure of the hydrostatic head is attained.
- Segregation effects due to significant differences in density between Ge and Si have to be considered during the growth of GeSi alloys. Experiments have shown that the orientation of the gravity vector is essential in respect to the segregation profile of GeSi Bridgman-grown crystals. In order to avoid gravitational effects it is essential to grow GeSi crystals under microgravity.
- Finally, the FZ growth of GeSi alloys is accompanied by interesting differences in the shape of the growth meniscus (compared to Ge or Si) due to the interaction between thermocapillary and solutocapillary effects. The specifics are discussed later but the full understanding of the interaction of these two effects, which might also influence detached growth, will require comparison between 1g and microgravity results.

Results

During the two years since the previous NASA Microgravity Materials Science Conference, most of the work supported by both the NASA and the DLR (German Space Agency) RDGS investigation has been published and is available for viewing or downloading from the [RDGS web site](#). This includes work carried out in Germany as well as in the United States.

Float zone work supported by the German RDGS is described, for example, in two Journal of Crystal Growth articles, [\[7\]](#) and [\[8\]](#).

The sessile drop measurements were completed and the results were presented at the Thirteenth International Conference on Crystal Growth (ICCG-13) in Kyoto, Japan in 2001 [\[9\]](#), and in two Journal of Crystal Growth articles, (for germanium) [\[10\]](#) and (for germanium-silicon alloys) [\[11\]](#).

Substantial additional progress was made on understanding the detached Bridgman growth process. The experimental part of this work was the subject of two additional presentations at the ICCG-13 on

germanium [12], and germanium-silicon alloys [13]. Both papers were accepted for inclusion in the proceedings issue of the Journal of Crystal Growth, (germanium) [14] and (germanium-silicon). [15]

A detailed, quantitative comparison of the etch pit density in germanium grown detached from the container wall and normally (attached to the container wall) was presented in a paper at the Thirteenth American Conference on Crystal Growth and Epitaxy (ACCGE-13) in Burlington, Vermont in 2001 [16], and a related paper was published in the Journal of Crystal Growth [17].

An overview of the investigation was presented at the Conference on International Space Station Utilization in 2001 [18].

This body of work, along with some yet to be published on the modeling of detached growth and the methods developed for characterizing the as-grown surfaces, enabled the investigation to successfully complete the Science Concept Review in December 2000.

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THE FEATURES OF SELF-ASSEMBLING ORGANIC BILAYERS IMPORTANT TO THE FORMATION OF ANISOTROPIC INORGANIC MATERIALS IN MICROGRAVITY CONDITIONS

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Hypothesis and Objective.

Materials with directional properties are opening new horizons in a variety of applications including chemistry, electronics, and optics. Structural, optical, and electrical properties can be greatly augmented by the fabrication of composite materials with anisotropic microstructures or with anisotropic particles uniformly dispersed in an isotropic matrix. Examples include structural composites, magnetic and optical recording media, photographic film, certain metal and ceramic alloys, and display technologies including flat panel displays. The new applications and the need for model particles in scientific investigations are rapidly outdistancing the ability to synthesize anisotropic particles with specific chemistries and narrowly distributed physical characteristics (e.g. size distribution, shape, and aspect ratio).

While there has been considerable progress toward developing an understanding of the synthesis of powders composed of monodispersed, spherical particles, efforts to prepare anisotropic nanoparticles are lagging. Amphiphilic molecules can be used to prepare either “water-in-oil” or “oil-in-water” micelles, and these organic “template” structures have been used to control the size of growing inorganic particles. Larger concentrations of the segregated phase leads to the formation of bilayer structures. In our laboratories, we have demonstrated that these anisotropic micellular structures can be used as templates to prepare anisotropic particles in both metallic and inorganic salt systems.^{1,2} This project aims to extend the methods that have been developed to other inorganic particle systems and to increase our level of understanding of how anisotropic particles are formed at lamellar templates.

As part of our studies, we make extensive use of model membrane systems prepared by Langmuir-Blodgett (LB) methods in order to efficiently survey possible template systems and establish the important chemical and geometric features of the templates that influence particle growth.³⁻⁶ Motivation for studying single-layer systems is two-fold. First, the chemical and structural properties of LB films are easily manipulated and characterized, allowing us to tailor the template system to the inorganic material being formed. Secondly, LB films on surfaces are less subject to the convectional shear, sedimentation, and agglomeration normally experienced by particles synthesized in the bulk solution. The surface confined bilayers can be used to establish how particle growth is limited by chemical and geometric considerations in the absence of convection and sedimentation effects. Results from the surface confined studies are continuously utilized in the design and choice of solution micellular systems as they are tailored to the desired inorganic materials. The program uses what is learned on the model systems to develop larger-scale preparations of the targeted inorganic materials at bilayer structures formed from “oil-in-water”

Keywords: semiconductors, metals, particles, anisotropic particles, new research

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segregated phase systems. It is these systems that will eventually lead to high yield, monodisperse preparations.

Justification for Microgravity Experiments.

The advantages of a microgravity environment for studying crystallization, nucleation and growth processes are well documented.^{7,8} In the present project, minimizing convection induced fluid shear and sedimentation in the microgravity environment should allow extended organic templates to form rather than fragments or “rafts” that result at normal Earth’s gravity. Convection limits the size of uniform template domains and also creates a non-uniform size dispersion. These imperfections in the template structures make it difficult to assess the role that the chemical and geometric identities of the template play in controlling particle size and dispersion. Reducing convection will also minimize the agglomeration of particles that are produced. Sedimentation is less of a problem than convection in the synthesis and processing of nanoscale particles or particles with nanometer scale in at least one dimension. Analysis⁹ demonstrates that the displacement due to gravity becomes less dominant as the particle size becomes smaller than about 0.25 μm . In contrast, sedimentation will begin to mask template effects as particle sizes increase beyond several hundred nanometers.

Metal Particles Formed in Free Standing Bilayer Templates.

Templating in free standing bilayers can be used to produce metal platelets as well as the semiconductors previously described.^{1,2} A variety of metallic platelets have been prepared in the water-octylamine system and the pentylamine/sodium dodecylsulfonate-toluene-water system including Ag, Ni, and Ag/Pd alloys of special interest to the electronics community. An image of an array of Ag platelets is shown in Figure 1. For each particle system, the surfactant system binary or ternary phase diagram has been determined in the presence of the relevant metal ions. Another complication is that after the platelets form, they must be protected by polymer dispersants to avoid aggregation of the metal particles. Poly(ethylene imine) was used to stabilize the metal particles shown in Figure 1.

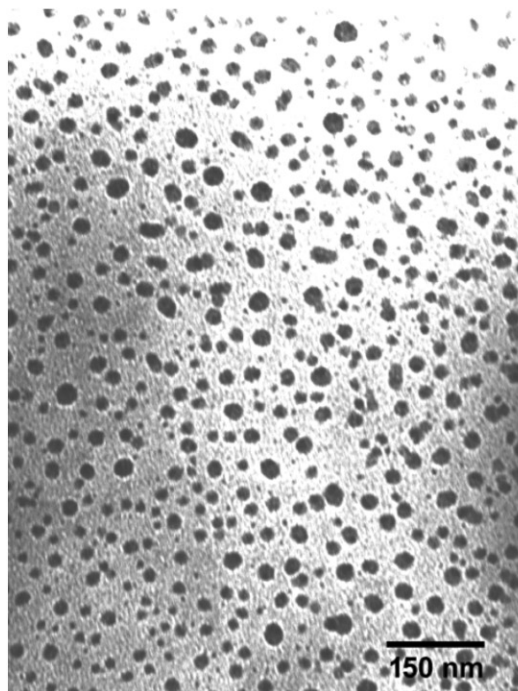


Figure 1. Ag particles formed from octylamine/water lamellar templates.

Mechanism of Particle Growth at Lamellar Templates.

The results on metal particles, along with our previous work on semiconductor systems, has now led us to a better, yet still incomplete, understanding of how the layered templates lead to anisotropic particles.¹⁻⁶ The organic assembly regulates particle growth through a combination of three different processes, which vary in relative importance for any given template/particle system. The first process is that of *confinement*. The template defines a space in which the particle can grow. A second process is through *specific interactions* between the template and the particle. Here, the template acts similarly to an adsorbate or poison in homogeneous preparations and stabilizes certain crystallographic faces at the template interface. Finally, the template controls *mass transport* to the growing particle. The diffusion is easier parallel to the template walls, and particles will grow in the directions that material is supplied.

We have observed that there are at least two general mechanisms that lead to the templating of two different classes of platelike particles. Each mechanism takes advantage of the processes of confinement, specific interactions and mass transport. The first we will call *crystal templating*, where the products are anisotropic single crystal particles. These particles result from a slow nucleation event, giving relatively few nuclei, and subsequent growth of the individual crystals.¹⁰ The anisotropic shape results from a combination of crystallization physics (determined from the solid-state structure of the material), specific interactions between the template and growing crystal faces, and directional transport of the reactant to the crystal.¹¹ Using micellar templates, we have observed single crystal metal platelets with dimensions up to several hundred nanometers and the size dispersion is broad. Using LB templates, particle sizes are somewhat larger, up to several microns, but there is also substantial polydispersity. The factors that control the size and polydispersity are not yet clear, yet we hypothesize that the size and uniformity of the template domains are important.

The second mechanism we will call *aggregate templating*. Here, the products are assemblies of smaller single crystal particles that aggregate in the shape of a platelet. The constituent particles need not have the same shape of the final product, and are most often spherical. The mechanism involves rapid nucleation followed by diffusion of the nuclei to form the platelets. The ultimate particle shape is limited by the vectorial diffusion of nuclei, which in turn is controlled by the shape of the template. At first glance, the influence of specific interactions on particle shape would appear to be less important in this mechanism, however, the chemical make-up of the template can affect the rapid nucleation event which in turn influences the polydispersity of the product. Particles formed through aggregate templating have a smaller dispersity than the single crystal particles. Preparations yielding particle sizes ranging from a few nanometers up to hundreds of nanometers have been developed for CdS in micelle templates.¹

Anisotropic Particle Suspensions.

A potential application of anisotropic particles are as mesogens in colloidal suspensions.^{12, 13} These complex suspensions of anisotropic inorganic particles are sometimes called “mineral liquid crystals,” because of the phase behavior and optical properties that parallel molecule and polymer-based liquid crystals. The electronic and chemical structures of inorganic extended solids could lead to hybrid materials that combine liquid crystalline behavior with traditional solid-state properties, such as conductivity or magnetism, which can be tuned through chemical synthesis.

We have experimented with anisotropic suspensions based on the family of layered metal hydroxides, $\text{Cu}_2(\text{OH})_{4-n}\text{X}_n$, where X is an anionic ligand.¹⁴ When X is an alkylcarboxylate, then organic suspensions

exhibit lyotropic behavior. The layered copper hydroxycarboxylates form as very small flat needles, a micron or less in length. The surface of the particles is hydrophobic as a result of the alternating organic/inorganic layered structure. The particles can be taken up in organic solvents, such as toluene, to yield anisotropic suspensions. The mixed organic/inorganic nature of the family of metal hydroxycarboxylates provides an opportunity to demonstrate the idea of combining properties into a single-phase material, as some examples are magnetic. We show, below, that the complex suspensions can be cast into transparent, anisotropic magnetic films.

Polycrystalline powders of the copper(II) hydroxycarboxylates can be dispersed in organic solvents such as toluene, xylene, or benzene. The resulting mixtures show different phase behavior that depends on the concentration range and temperature. The general trend for the copper(II) hydroxystearate particles dispersed in toluene at ambient temperature, is shown in Figure 1. At low concentration, below about 1.5%, the particles do not disperse throughout the solvent, but rather there is segregation of the suspended particle phase and the clear, pure solvent. If viewed through cross polarizers, the suspended particle phase is birefringent, while the pure solvent phase is isotropic. As the concentration of polycrystalline solid is increased, a gelatinous phase results that is also birefringent (Fig. 2).

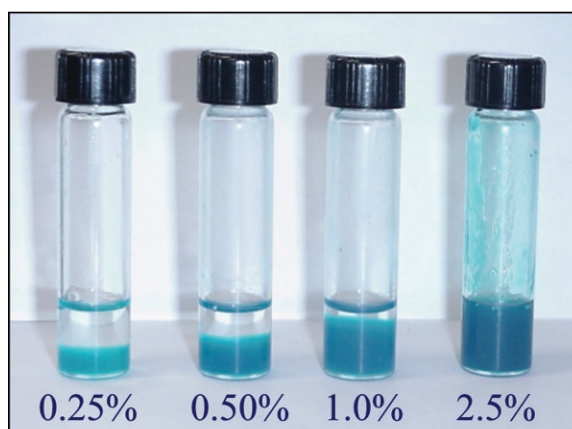


Figure 2. Copper(II) Hydroxystearate Suspension in Toluene at Different Weight Percents.

An optical micrograph of the gel phase, observed through untreated glass plates and obtained through crossed polarizers, is shown in Figure 3. The optical birefringence shows a marble texture characteristic of liquid crystalline phases. Upon heating either the biphasic or gel phases, an isotropic solution is obtained above a clear point. For the copper(II) hydroxystearate the clear point is $70\text{ }^{\circ}\text{C} \pm 1$ for all compositions. The birefringent domains are recovered upon cooling through the clear point. Also consistent with the characteristic fluidity associated with liquid crystalline behavior, the birefringent domains change shape and size in response to external stimuli such as shear or uneven pressure.

Oriented Films

The suspensions can be cast onto a surface that, after solvent evaporation, leaves an oriented thin film. For example, casting the copper(II) or nickel(II) hydroxystearate suspensions onto Mylar, followed by lifting off of the surface, results in self-standing, flexible, transparent films (Figure 4a). Since the solvent has been removed, the thin films are comprised of only the starting powder, but are now transparent because the individual crystallites are aligned, leading to decreased scattering. A scanning electron microscope image (Figure 4b) shows that the texture of the film is very homogeneous, and the particles show a preferential orientation with the long axis parallel to the surface of the film.

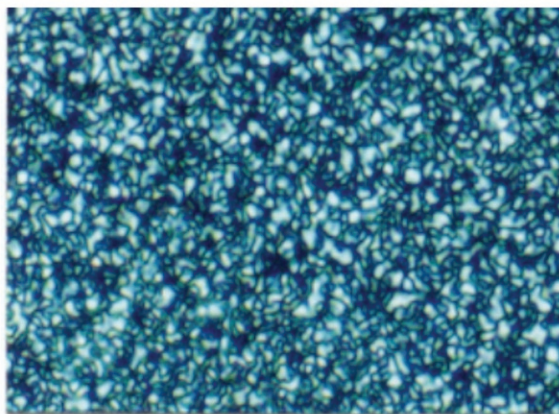


Figure 3. Crossed polarized micrograph of a copper hydroxystearate gel (5% weight). A marble texture with black domain boundaries can be seen. The picture area has dimensions $97 \times 58 \mu\text{m}^2$.

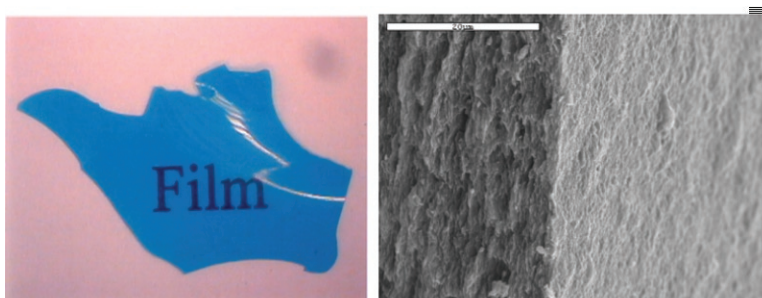


Figure 4. (A) a free-standing film of copper(ii) hydroxystearate set on top of the word "film." The film was cast from a nematic gel in toluene. (B) an SEM image of the edge of a copper(ii) hydroxystearate film showing texture that results from the alignment of the particles parallel to the surface, the scale bar corresponds to $20 \mu\text{m}$.

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SURFACE TENSION AND VISCOSITY OF SCN AND SCN-ACETONE ALLOYS AT MELTING POINTS AND HIGHER TEMPERATURES USING SURFACE LIGHT SCATTERING SPECTROMETER

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Succinonitrile has been and is being used extensively in NASA's Microgravity Materials Science and Fluid Physics programs and as well as in several ground-based and microgravity studies including the Isothermal Dendritic Growth Experiment (IDGE). Succinonitrile (SCN) is useful as a model for the study of metal solidification, although it is an organic material, it has a BCC crystal structure and solidifies dendritically like a metal. It is also transparent and has a low melting point (58.08°C). Previous measurements of succinonitrile (SCN) and alloys of succinonitrile and acetone surface tensions are extremely limited. Using the Surface Light Scattering technique we have determined non invasively, the surface tension and viscosity of SCN and SCN-Acetone Alloys at different temperatures.

This relatively new and unique technique has several advantages over the classical methods such as, it is non invasive, has good accuracy and measures the surface tension and viscosity simultaneously. The accuracy of interfacial energy values obtained from this technique is better than 2% and viscosity about 10 %. Succinonitrile and succinonitrile-acetone alloys are well-established model materials with several essential physical properties accurately known - except the liquid/vapor surface tension at different elevated temperatures. We will be presenting the experimentally determined liquid/vapor surface energy and liquid viscosity of succinonitrile and succinonitrile-acetone alloys in the temperature range from their melting point to around 100°C using this non-invasive technique. We will also discuss about the measurement technique and new developments of the Surface Light Scattering Spectrometer.

Keywords: interfacial energy, succinonitrile, surface light scattering spectroscopy, surface tension, viscosity, characterization

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DEVELOPMENT OF A MONTE CARLO RADIATION TRANSPORT CODE SYSTEM FOR HEDS: STATUS UPDATE

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Abstract

Modifications of the Monte Carlo radiation transport code HETC are underway to extend the code to include transport of energetic heavy ions, such as are found in the galactic cosmic ray spectrum in space. The new HETC code will be available for use in radiation shielding applications associated with missions, such as the proposed manned mission to Mars. In this work the current status of code modification is described. Methods used to develop the required nuclear reaction models, including total, elastic and nuclear breakup processes, and their associated databases are also presented. Finally, plans for future work on the extended HETC code system and for its validation are described.

I. Background

Galactic cosmic rays (GCR) and occasional, but intense, fluxes of solar energetic particles (SEP) present severe radiation hazards to manned planetary exploration, such as the proposed human mission to Mars. Although the major uncertainty in estimating crew risk to these radiations is related to the biological response to HZE (high charge and energy) ions in the GCR environment, a significant uncertainty (possibly a factor of two) may be contributed by current radiation transport models and methods used in predicting secondary particle fluxes and their spectra behind shielding¹. The current uncertainty estimates are so large that simply adding more shielding to account for them imposes severe weight penalties and is not a viable option. Therefore research directed toward reducing the uncertainties is required.

In this work we are developing a radiation transport code system for deep space applications based on Monte Carlo methods. This is the methodology most commonly used in a variety of technical areas for high-energy radiation transport, but has not been previously applied in addressing these space radiation issues. This transport method has inherent capabilities - namely, 3-D transport, modular programming, and detailed output - that are very important for human exploration applications. The code used herein is the High Energy Transport Code (HETC).²

Most of the work involves extending HETC to include heavy-ion transport, which is needed for human exploration and development of space (HEDS) applications to transport the heavy-ion component of the GCR environment. This is being accomplished by incorporating heavy-ion nuclear collisions models into HETC. Also, we plan to update the nucleon/pion nuclear collision model in HETC to incorporate the most accurate models currently in use worldwide. This new heavy-ion/nucleon-meson transport code, HETC/HEDS, will be coupled with other transport codes specialized for low-energy neutron transport (MORSE) and electron-photon transport (EGS) to provide a full-capability Monte Carlo radiation transport “code

Keywords: space radiation, shielding, radiation transport, Monte Carlo, nuclear

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system” for HEDS applications. The following sections describe the work carried out to date in performing these modifications.

II. Needed Modifications to HETC

While HETC has had wide application, it is not suitable for all HEDS applications in its present form because it does not incorporate the transport of heavy ions, which are an important component of the GCR environment for HEDS radiation protection assessments. Therefore, a major part of the work being carried out focuses on extending HETC to include heavy ion nuclear interaction models and the associated software modifications needed for heavy ion tracking.

Unfortunately, a single, complete heavy-ion nuclear-collision model, capable of rapidly and accurately predicting double differential energy-angle secondary spectra for all of the ions, energies, and target materials of interest, does not exist. Therefore, we resort to using several models that address different aspects of nucleus-nucleus collisions. As GCR ions are transported, the distance to the next nuclear interaction must be determined. This requires knowing total cross sections (sum of elastic and reaction cross sections) for nucleus-nucleus collisions over energies ranging from several MeV/nucleon up to several GeV/nucleon in order to estimate the mean free path (usually several cm) for nuclear collision. The methodology used to calculate these cross sections is described in the next section. Since these heavy ions are highly charged (ionized), they also lose energy through a myriad of collisions with orbital electrons of the atoms in the target medium. This energy loss must also be accounted for in the transport code. Once the collision occurs, it must be determined if it is an elastic or nonelastic collision. Nonelastic collisions at typical GCR energies are usually fragmentation or spallation events, where one or both nuclei breakup as a result of the collision. Since no single model exists that specifies the directions and energies of all secondary particles produced in collisions of all incident and target nuclei at all energies of interest, a hybrid one is being developed, as discussed in the next section.

Software interfaces for the extended version of HETC containing heavy-ion transport and updated nucleon and pion collision models (designated here as HETC/HEDS) must be provided so that it can be coupled with low-energy neutron transport and electron-photon transport codes. This provides a complete Monte Carlo transport code system for HEDS, capable of transporting all particle types (protons, heavy ions, neutrons, pions, muons, electrons, positrons, and photons) over all energy ranges of interest for GCR (and SEP) induced environments.

The nuclear models to be incorporated into HETC/HEDS are not applicable for low-energy (<20 MeV) neutron interactions, but several well-tested and widely used transport codes are available that provide neutron transport from 20 MeV down to thermal energies and take into account the production and transport of secondary gamma-rays from inelastic scattering and capture reactions. We plan to deliver the code system with MORSE³ as the low-energy neutron transport code although the interface with HETC/HEDS will be such that other codes, such as the Los Alamos MCNP code, could also be used.

The HETC/HEDS code system will also allow coupling with the EGS (Electron-Gamma Shower) Monte Carlo code⁴ for (optionally) calculating the electromagnetic cascade induced by neutral-pion decay. The HETC/HEDS, MORSE, and EGS transport codes will be interfaced with a common 3-D combinatorial geometry (CG). The CG methodology allows complex configurations to be modeled based on logical combinations of simple volumes (spheres, boxes, cones, etc.). This type of geometry module has been well tested and is often used with these transport codes.

We will also provide the HETC/HEDS-MORSE-EGS code system for HEDS applications with a general source module for ambient GCR and SEP proton and heavy-ion environments. This module will allow users to specify GCR and SEP sources to be used as input. There are two reasons for incorporating this specialized source module: as a convenience to users, and because special techniques are needed to ensure that the Monte Carlo energy selections from spectra over the large GCR energy range (~10 MeV/nucleon - 100 GeV/nucleon) are made accurately.

III. Status of Modifications

Modifications to the HETC code are in progress. Those completed or nearly completed include: 1) The range energy tables for all nuclides have been incorporated and debugging processes have begun; 2) The interfaces with the cross sections and collision models have been defined and programmed into the heavy ion transport system; 3) The geometry module has been interfaced with the heavy ion transport module. Note that the interfaces mentioned in 2) still require the appropriate collision models/data as inputs. These data needs are currently being addressed as described below.

Nuclear Database Development

Nuclear databases needed include total cross sections, which enable collision mean free paths to be determined, and double-differential secondary particle production cross sections (energy and angle for every secondary particle). A suitable model for the total cross section has been developed for use in the HETC/HEDS code system. It is described below. Double-differential cross sections for secondary particle production do not exist for most projectile-target-beam energy combinations of interest, either as experimental data or as theoretical formulations. Hence, models must be adapted from other applications or developed specifically for use in this code system. The present status of fragmentation database development is also described below.

1. Total Cross Sections. Since there are essentially no measured data in existence for total cross sections from nucleus-nucleus collisions, they must be modeled using nuclear theory. During the 1970's and early 1980's, quantum mechanical optical potential models, based on multiple scattering theory, were developed at NASA Langley Research Center⁵⁻⁷ for use in generating databases of nucleon-nucleus and nucleus-nucleus total and reaction cross sections for GCR heavy ion transport. The predicted cross sections were found to be in excellent agreement with measurements of total and reaction cross sections for nucleon-nucleus collisions and for nucleus-nucleus reaction cross sections for energies above ~50 MeV/nucleon. At lower energies there were tendencies for both the predicted total and reaction cross sections to be smaller than the measured values, especially for incident nucleons and light ions such as deuterons. As the projectile kinetic energies decreased, the differences between predicted and measured values increased. Nevertheless, tabulated values of these cross sections for energies between 25 MeV/nucleon and 22.5 GeV/nucleon were published.^{6,8,9}

In subsequent work at NASA Langley, Tripathi developed a semiempirical formulation of nuclear reaction cross sections which was accurate down to energies as low as ~ 1 MeV/nucleon.^{10,11} Hence, it was decided to improve the low energy predictions for the total cross sections to be used in HETC by scaling the reaction cross sections of Tripathi using ratios of the total-to-reaction cross sections obtained from the earlier quantum mechanical optical model⁷ developed at NASA Langley. Thus, the total cross section is estimated from

$$\sigma_{\text{TOT}} = R \sigma_{\text{R}}(\text{Tripathi}) \quad (1)$$

where R is the optical model cross section ratio given by

$$R = \sigma_{\text{TOT}}(\text{optical})/\sigma_{\text{R}}(\text{optical}) \quad (2)$$

Sample results are displayed in Figures 1 and 2 for carbon-carbon scattering and for iron-lead scattering.

These nuclear systems were chosen for illustrative purposes since they represent systems involving lighter and heavier pairs of nuclei of interest in GCR transport. Displayed are the results from Townsend et al⁸ (labeled “Optical”) and the predictions obtained using Eq. (1) (labeled “This Work”). Note that the cross

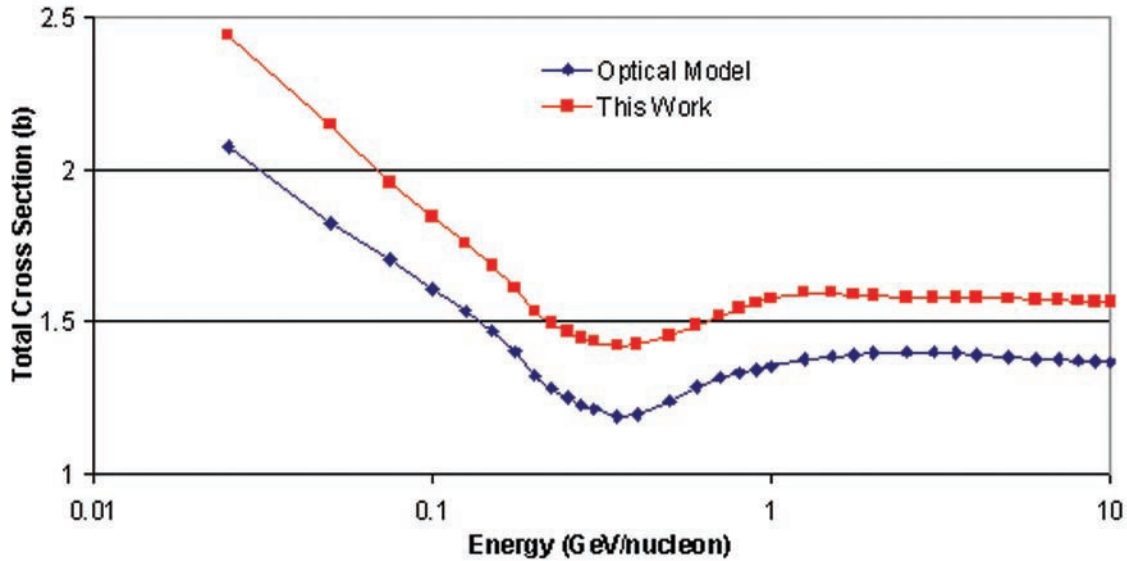


Figure 1. Total cross sections for carbon – carbon collisions as a function of energy.

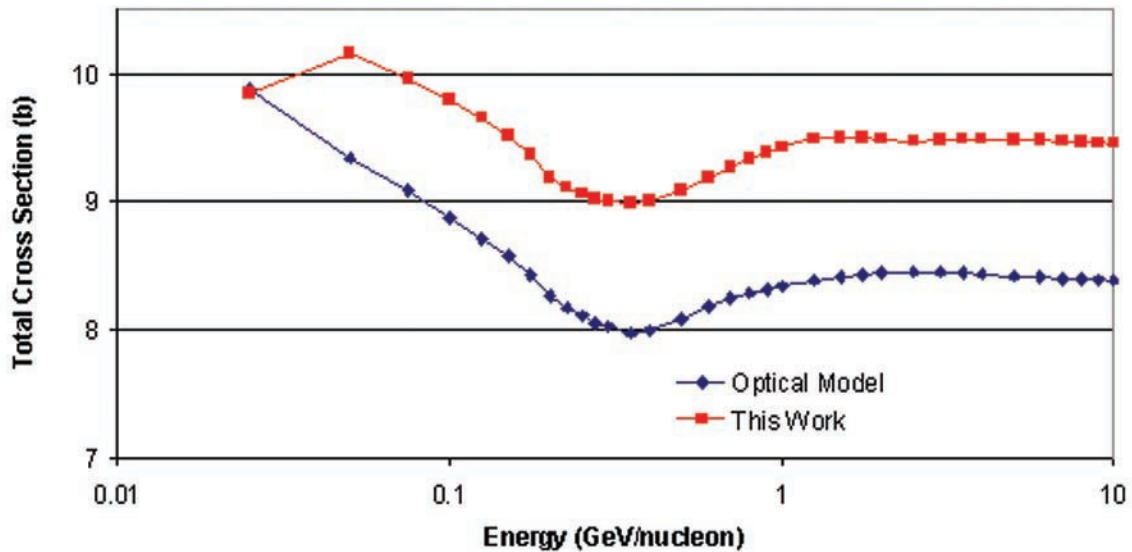


Figure 2. Total cross sections for iron – lead collisions as a function of energy.

sections exhibit strong energy dependence, especially at energies lower than ~ 1 GeV/nucleon. Hence, simple energy independent formulas or parameterizations, which are sometimes used in the literature, are likely to be inaccurate. The formalism represented by the above equations has been incorporated into a FORTRAN module for inclusion in the HETC/HEDS code system.

2. Heavy Ion Fragmentation. At present there is no one (single) event generator capable of predicting the directions and energies of all secondary particles produced in a fragmentation or spallation reaction, within a reasonable period of time, for all combinations of projectile ion, target nucleus and incident particle energy

present in the GCR spectrum. Most of the models used in present day heavy ion transport codes predict inclusive cross sections (total yields) of each fragment produced in the collision. Several models have been developed for predicting the fragmentation yields (total cross sections) for secondary particles created by the breakup of a heavy-ion projectile striking a target nucleus¹²⁻¹⁴ for space radiation transport applications. Accurate cross sections for heavy fragment production are produced by the optical potential fragmentation model of Townsend and collaborators¹⁴. However, this model is still under development and cannot be used at present to generate yields of nucleons and light ions. This same shortcoming exists with the semi-empirical parameterization of Silberberg and Tsao¹³.

Perhaps the best model for this purpose, currently described in the literature, is the NUCFRG2 model developed at NASA Langley Research Center.¹² It accounts for all the yields of secondary light ions and heavy ion fragments produced by a nucleus-nucleus collision. NUCFRG2 is currently used to generate fragmentation databases for the publicly released 1-D deterministic GCR transport code HZETRN developed at NASA Langley.¹⁵ Table 1 displays representative isotope production results for 1 GeV/nucleon carbon colliding with carbon targets. Note that summing these cross sections gives a result that is greater than the total reaction cross section for the collision. This is because the cross sections are inclusive, which means that the results for light ions ($Z \leq 2$) include multiplicity effects. Corrections to the multiplicities resulting from the inclusive nature of the calculations must be incorporated since exclusive cross sections are needed. The isotope yields predicted by the projectile fragmentation models discussed above are in the form of total cross sections or yields. Hence, they are invariant with respect to reference frame. Therefore, cross sections for producing target fragments can be obtained by interchanging the projectile and target nuclei at the same kinetic energy per nucleon.

Table 1. NUCFRG2 Output for 1 GeV/nucleon carbon-carbon collisions

Fragment Charge	Fragment Mass	Production Cross Section (mb)	Fragment Charge	Fragment Mass	Production Cross Section (mb)
6	11	5.290E+01	3	6	2.862E+01
6	10	3.538E-01	3	5	0.000E+00
6	9	2.730E-03	3	4	0.000E+00
6	8	2.300E-06	3	3	0.000E+00
5	11	5.312E+01	3	2	0.000E+00
5	10	5.457E+01	2	9	4.610E-06
5	9	3.074E+00	2	8	3.350E-05
5	8	1.600E-02	2	7	0.000E+00
5	7	0.000E+00	2	6	3.674E-01
5	6	3.750E-06	2	5	0.000E+00
4	11	0.000E+00	2	4	1.512E+02
4	10	3.299E+00	2	3	1.173E+01
4	9	1.315E+01	2	2	0.000E+00
4	8	3.452E+00	2	1	0.000E+00
4	7	1.895E+01	2	0	0.000E+00
4	6	7.850E-02	1	7	0.000E+00
4	5	0.000E+00	1	6	3.330E-05
4	4	0.000E+00	1	5	0.000E+00
3	11	0.000E+00	1	4	0.000E+00
3	10	2.520E-03	1	3	0.000E+00
3	9	3.420E-02	1	2	6.189E+01
3	8	1.061E-01	1	1	4.479E+03
3	7	2.053E+01	1	0	0.000E+00

Since secondary particle directions of travel must also be specified, we use momentum distribution models to select the directions and energies of the collision fragments. At high energies secondary ion fragments of GCR particle interactions typically travel in the direction of the incident ion with some slight angular dispersion and momentum loss resulting from the momentum transfers that occur during the collision. These fragment momentum distributions, which are experimentally found to be Gaussian in shape, can be obtained from phenomenological models such as those due to Tripathi and Townsend¹⁶ or due to Tsao and collaborators.¹⁷ The Tsao parameterization is used in this work. It is more complete than the other model in that it estimates momentum components in both the parallel and transverse directions as well as the widths of these momentum distributions. Typical results for two different fragments resulting from a 1 GeV/nucleon carbon - carbon collision are shown below in Table 2. Note that the model presents momentum distribution in both the laboratory frame (3-D Analysis) and in the projectile nucleus rest frame (Beam Analysis). Symbols used in the table include KE (kinetic energy), S_KE (standard deviation

Table 2. Summary of Momentum Output from Tsao et al Model¹⁷

SYSTEM: (12, 6) + (12, 6) --> (8, 4) + X.		SYSTEM: (12, 6) + (12, 6) --> (4, 2) + X.	
Projectile spallation product:		PROJECTILE SPALLATION PRODUCT:	
*** 3-D Analysis ***:		*** 3-D ANALYSIS ***:	
Nominal KE [lab]:	1.0000E+03 MeV/ nucleon	Nominal KE [lab]:	1.0000E+03 MeV/ nucleon
Estimated KE:	9.7786E+02 MeV/ nucleon	Estimated KE:	9.6210E+02 MeV/ nucleon
Estimated KE loss:	2.2139E+01 MeV/ nucleon	Estimated KE loss:	3.7905E+01 MeV/ nucleon
Estimated KE loss (%):	2.21E+00	Estimated KE loss (%):	3.79E+00
Estimated S_KE (%):	5.35E+00	Estimated S_KE (%):	8.72E+00
*** Beam Analysis ***:		*** BEAM ANALYSIS ***:	
<PII> in Proj. Frame:	-6.2217E+01 MeV/c	<PII> in Proj. Frame:	-7.3067E+01 MeV/c
S_PII in Proj. Frame:	1.9738E+02 MeV/c	S_PII in Proj. Frame:	1.9738E+02 MeV/c
S_Ppe in Proj. Frame:	3.9476E+02 MeV/c	S_Ppe in Proj. Frame:	3.9476E+02 MeV/c
<BII> in Proj. Frame:	-8.33E-03	<BII> in Proj. Frame:	-1.56E-02
Estimated KE loss:	1.1932E+01 MeV/ nucleon	Estimated KE loss:	1.8944E+01 MeV/ nucleon
Estimated KE loss (%):	1.19E+00	Estimated KE loss (%):	1.89E+00

of KE), <PII> (mean value of momentum parallel to beam), S_PII (standard deviation of PII), S_Ppe (standard deviation of the transverse component of momentum; note that the transverse momentum in the projectile rest frame is zero), and <BII> (longitudinal component of the relative velocity as a fraction of the speed of light). The Tsao model is currently being used to generate a database, which will be incorporated into a fragmentation module in the HETC/HEDS code, either in tabular or parameterized form.

3. Nucleon Production. A model for neutron production in high-energy heavy ion collisions by Cucinotta, Townsend, and Wilson¹⁸ is currently being developed under a separate project funded by the NASA Microgravity Materials Science Program. The model is also capable of predicting proton emission in high-energy heavy ion collisions as well. Work on this new nucleon production model is nearly complete. When completed it will be used to generate nucleon emission spectra (energy and angle) for the HETC/HEDS code system.

IV. Conclusions

The current status of developments in extending the HETC code to transport galactic cosmic ray heavy ions for space radiation transport and shielding applications has been reviewed. Efforts to develop modules describing the nuclear interactions of these ions, and their transport through matter have been presented. Sample results for total cross sections and momentum distributions were shown. Future work needed to complete the development of the HETC/HEDS code system was also discussed.

Acknowledgments

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INTERFACE PATTERN SELECTION CRITERION FOR CELLULAR STRUCTURES IN DIRECTIONAL SOLIDIFICATION (IPSIDS)

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Objectives

The central focus of this flight-definition investigation is to establish key scientific concepts that govern the selection of the interface patterns during the directional solidification of alloys. The critical scientific concepts in the selection of the interface patterns will be addressed first and then the results of the ground-based experimental studies in the Al-Cu alloys will be presented.

For directional solidification of an alloy, the key problem is to establish the criteria that dictate the selection of a unique solution, or a certain narrow set of solutions, for cellular and dendritic patterns. The extensive ground-based experiments on the three-dimensional patterns show significant disorder due to the presence of gravity-induced fluid flow, so that microgravity experiments are needed to obtain benchmark data in which gravity-induced fluid flow is negligible. The results of the theoretical model and the parameters to be measured for low gravity experimental data will be discussed to obtain quantitative understanding of the fundamental physics of pattern formation and to establish a reliable theoretical framework for the prediction of the pattern formation.

The ground-based results to establish the experimental matrix, to determine the physical constants of the system and to analyze low gravity experiments will be presented. The experimental matrix was determined by developing a new technique in which diffusive growth could be obtained in thin samples, i.e., $<\phi 1.0\text{mm}$ for Al-4.0wt%Cu alloys. We have developed new experimental techniques to measure two critical system parameters: anisotropy in interfacial energy and the solute diffusion coefficient in the liquid. The anisotropy for Al-4.0wt%Cu alloy is 0.0098 ± 0.0008 with 95% confidence interval, which is the first experimentally measured value for nearly isotropic metallic systems. The intrinsic solute diffusion coefficient in liquid was found to be $2.4 \times 10^{-9} \text{ m}^2/\text{s}$, which is significantly smaller than the previous results that were measured in larger samples ($>\phi 2.0\text{mm}$) and thus were influenced by fluid flow. We have experimentally determined the transient time for steady-state primary arm evolution through three different analyses of the microstructure: Minimum Spanning Tree (MST), Voronoi Polygons and distribution of primary spacings. We also devised the method to analyze the effect of quenching on interface shape and developed the reconstruction techniques for three-dimensional shapes of the array quantitatively analyze flight experimental results on the cell/dendrite shapes.

Introduction

During the directional solidification of alloys, the solid/liquid interface undergoes several transitions as the experimental parameters are varied [1-3]. The most common patterns in commercial processing of

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materials are cellular and dendritic patterns. One of the key issues in the fundamental understanding of the formation of these patterns is that the diffusive transport models give infinite number of solutions whereas only finite number of patterns are observed experimentally. Thus the understanding of the fundamental physics that determines the selection of these specific patterns is crucial in predicting the microstructure development. The key problem is then to quantitatively establish the criterion and the associated physics that dictates this selection of a certain narrow set of solutions.

For cellular growth, the interaction of diffusion fields between the neighboring cells is significant so that the cellular spacing influences the shape of the interface and all the other cell characteristics such as the tip radius and the length of the mushy zone [4,5]. Experimental validation of the diffusive growth models has not been possible due to the difficulty in obtaining diffusive growth conditions in bulk samples under terrestrial conditions since cellular growth occurs under conditions where convection effects are dominant. Thus, a rigorous test of cellular and dendritic models requires precise experiments on 3-D arrayed growth in bulk samples. A full-scale numerical modeling has been conducted to disclose the fluid flow pattern in the melt [6,7] and experimental results will be presented to establish the dominant effect of convection for cellular microstructures in samples where a large number of cells is required for a quantitative analysis. The use of capillary sample solidification technique makes it possible to study cell/dendritic growth under diffusive growth process [8-11]. Cellular growth requires very fine samples in which only few individual cells can develop. To obtain a finite number of cells, a larger sample diameter is required where significant convection in the melt is present. Consequently, microgravity experiments are planned to obtain benchmark data for the selection of cellular shapes under diffusive growth conditions.

Two critical system parameters remain unclear: anisotropy of S/L interfacial energy, ϵ_4 , and the intrinsic diffusion coefficient in liquid, D_L . There is no report for the former; and for the latter the literature cited value ranges from 3 to $5 \times 10^{-9} \text{ m}^2/\text{s}$ [12, 13, 14]. Since the values were derived from the composition profile in a sample larger than 2.0mm , convection is inevitable; therefore the quoted data do not represent the intrinsic value. With the capillary sample solidification technique, we are able to derive the diffusion data without the effect of fluid flow. For metallic sample, the interface morphology is examined by quenching and polishing the sample. The critical question we have addressed is: can the quenched interface represent the original solid/liquid interface prior to quenching? We thoroughly studied this through systematic composition measurement and the interface advance in the quenching process was quantitatively characterized.

Ground-based experimental research

1. *Microstructure in a bulk sample*

1.1 Macroscopic L/S interface shape. It is generally assumed that heat flow in a DS process is unidirectional, i.e., perpendicular to L/S interface, and that macroscopic L/S interface shape is flat. However in a common design of a DS unit with radial heating and cooling arrangement, a radial temperature gradient always exists that can lead to a curved L/S interface. Figure 1(a) shows a quenched stationary L/S interface of Al-4.0wt%Cu in our directional solidification unit and it is clear that the interface is not flat but slightly convex, indicating a radial temperature difference [8]. This is the driving force when solidification process starts since the hot liquid near the periphery region is more buoyant and tends to rise.

Figure 1(b)-(d) shows the quenched L/S interfaces in Al-4.0 wt% Cu samples of different diameters grown at the same velocity and quenched at the same growth distance. The interface shape in a sample of $\phi 5.0 \text{ mm}$ (Fig. 1(b)) is highly curved and convex. Figs. 1(c) and 1(d) show the interface shapes in reduced sample sizes, i.e., 1.0

mm, and 0.6 mm respectively, and the interface convexity is observed to decrease significantly. The enhanced interface convexity is solely from the convection in the liquid that carries the rejected solute at the interface radially outwards and generates the radial composition profile toward the periphery of the sample [9].

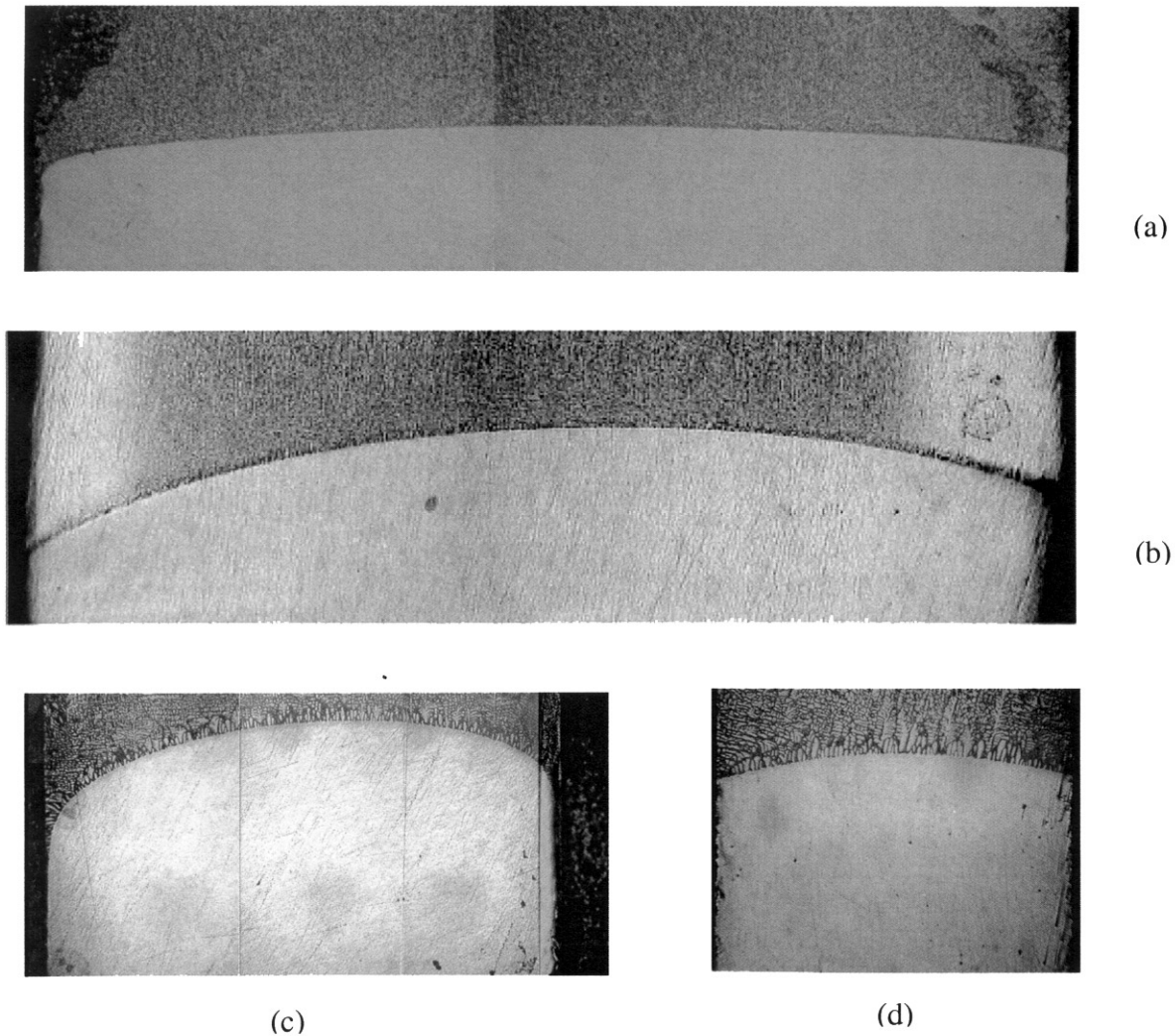


Fig. 1. Quenched interface shape for different sample sizes of Al-4.0 wt%Cu sample ($G=7.0\text{K/mm}$)
 (a) $\phi 5.0\text{mm}$, stationary; (b) $\phi 5.0\text{ mm}$, $V=0.4\text{ }\mu\text{m/s}$
 (c) $\phi 1.0\text{ mm}$, $V=0.4\text{ }\mu\text{m/s}$, (d) $\phi 0.6\text{ mm}$, $V=0.4\text{ }\mu\text{m/s}$

1.2. Mixed structures on a growth front. Since convection in the melt generates non-uniform composition distribution radially it has been observed that different microstructures may develop across the section of the sample. Figure 2(a) shows a sample that is planar in the central region, but cellular at the periphery. Since G and V are the same in a given experiment, these studies provide valuable information on the interface morphologies developed due to the variation in interface composition.

To understand the formation of a mixed microstructure, compositions in the liquid at a growing interface were determined across the sample, and the results are shown in Fig. 2(b) respectively. The composition continually increased from the center to the periphery, i.e., radial segregation occurred, which is consistent with the mode of convection due to radial temperature gradient.

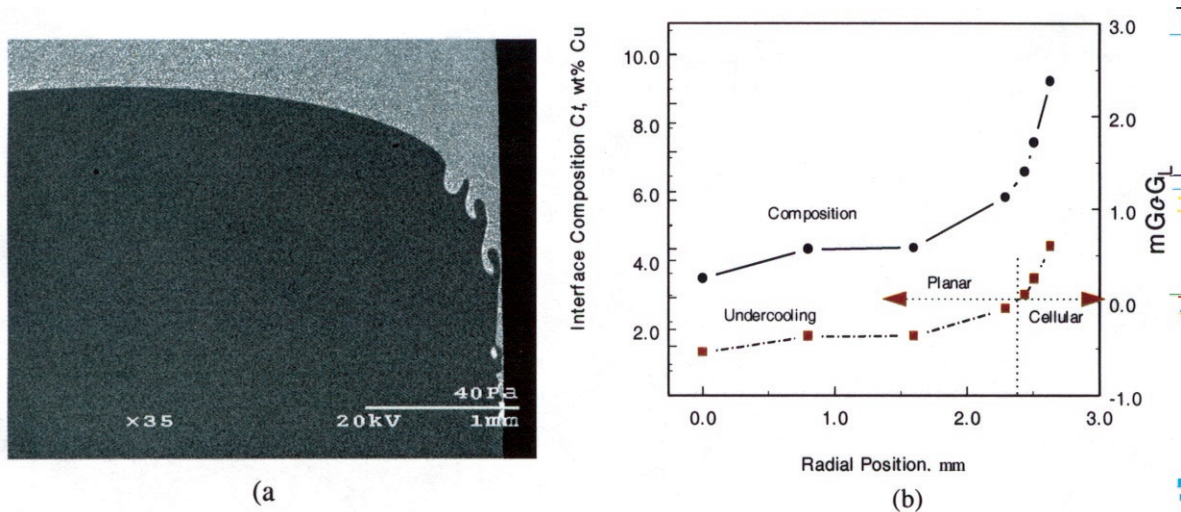


Fig. 2(a). Mixed planar/cellular interface morphology ($G=6.5 \text{ K mm}^{-1}$, $V=0.45 \text{ } \mu\text{m s}^{-1}$)
 2(b) Measured interface composition as a function of radial position. Superimposed in the figure is the further calculation of interface undercooling parameter mG_c-G_L

The mixed microstructures are sensitive to the growth conditions. The G/V ratio for Fig. 2 is less than the critical ratio for Mullins-Sekerka stability, so the overall cross-section should be cellular. However, in this large sample ($\phi 5.5\text{mm}$), the local composition in the central region is lower than the nominal alloy composition and the periphery region is much higher, thus the central region was planar whereas the periphery was cellular. Further calculation of the constitution undercooling parameter (mG_c-G , G_c : concentration gradient at the growing interface) based on the measured composition is also included in Fig 2(b) and it clearly shows that the transition from planar to cellular agrees with the Mullins-Sekerka stability analysis if the local composition is considered.

2. Establishment of diffusive growth in a capillary sample

Numerical modeling has predicted that for Al-4.0wt%Cu, when the sample diameter is less than 1.0mm, the growth process is dominated by solute diffusion [8]. It has been observed through composition measurement that composition profile in a $\phi 1.0$ and $\phi 0.6\text{mm}$ sample is the same within the experimental error and significantly different from the bulk sample at the same growth conditions [8,9, 15].

Figure 3(a) shows the longitudinal section of directionally solidified Al-4.0wt%Cu sample with a $\phi 0.8\text{mm}$ thin tube immersed in the center which was quenched at solid fraction $f_s=0.3$. The morphology in the thin sample is clearly cellular, while the interface of the bulk part is highly curved but planar in the region close to the thin sample. In order to establish the presence of steady state in a thin sample, another experiment was carried out under the same condition (G , V and C_0) as in Fig. 3(a), but with a larger solid fraction, $f_s = 0.49$. Since the eutectic interface undercooling is negligible at low growth rates used in this study, the eutectic interface gives a reference temperature, $T_E = 548^\circ\text{C}$ in the Al-Cu system. The position of the cellular and planar interface in the two samples from the eutectic interface location can now be measured, and the results are given in Table 1. The distances between the cell tip in the thin sample and the eutectic interface in these two experiments with different f_s 's were found to be the same that confirmed that steady state conditions were reached in the thin samples. Since the bulk is still dominated by convection, the interface, though planar, has not reached a steady state. The interface temperature during the transient will be higher than the solidus temperature so that the planar front temperature can be higher than the steady state cell tip temperature, as observed in the experiment.

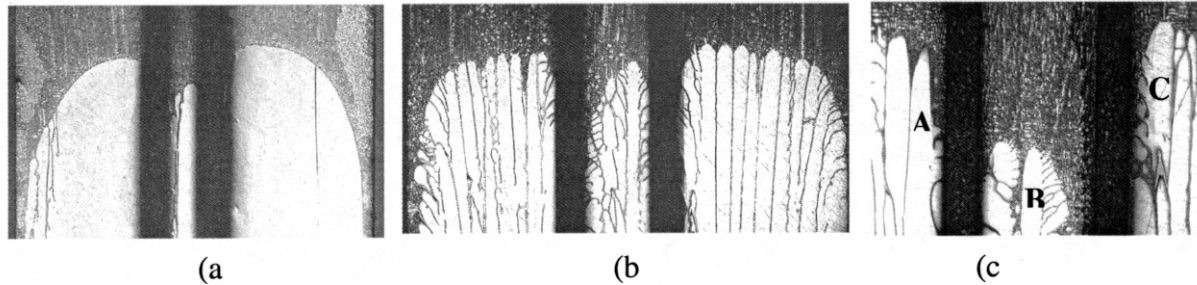


Fig. 3 (a) A cellular interface inside a $\phi 0.8$ mm tube, whereas a planar interface is observed in the outer region, $V = 0.9 \mu\text{m/s}$, $G = 7.0$ K/mm. (b) A dendritic interface forms inside the thin tube, whereas cellular structure is observed in the outer region. $V = 6.0 \mu\text{m/s}$, $G = 7.0$ K/mm. (c) An enlarged view of the difference in interface positions in the thin sample and in the outer region for $V = 5.0 \mu\text{m/s}$ and $G = 7.0$ K/mm. The bulk is $\phi 5.5$ mm and the thin sample is $\phi 0.8$ mm

Sample	Total Length, mm	Solidified length, mm	Solid fraction, f_s	$X_T^* - X_E^*$ mm	$X_B^* - X_T$ mm
#1	165	53	0.3	10.60	0.55
#2	145	71	0.49	10.65	0.42

* X_T : Interface position in the thin sample, X_E : Eutectic interface position, X_B : interface position of the surrounding bulk.

Figure 3(b) shows the formation of dendrites in the thin sample, whereas cells grow in the neighboring bulk region. This again indicates that the convection stabilizing the growing interface and shifts cellular to dendrite transition to higher velocities. Moreover, the position of the interface inside the thin sample is lower than that in the outer region even though the growth is dendritic in the thin sample, and the difference in position increases as the velocity is reduced, as seen in Figs. 3(b) and 3(c).

3. Experimental matrix for microgravity experiments

With the thin sample solidification technique, systematic experimental study has been conducted to determine the morphological evolution for Al-4.0wt%Cu for different growth conditions and this has been shown in Fig. 4(a). In comparison, the morphology in a bulk sample ($\phi 5.0$ mm) is shown in Fig. 4(b) in which planar, cellular and dendritic morphology may develop in the sample; while for the thin sample, no planar front was ever observed for the growth conditions that was explored in this study.

Since the morphology evolved in the thin sample is controlled by diffusion, figure 5(b) can be used as a guide for the design of future microgravity experiments. At each temperature gradient, the velocity should be chosen such that the growth morphology covers the pure cellular, cellular/dendritic coexistence and pure dendritic regime so that the transition condition from cells to dendrites can be unambiguously determined from the microgravity experiments.

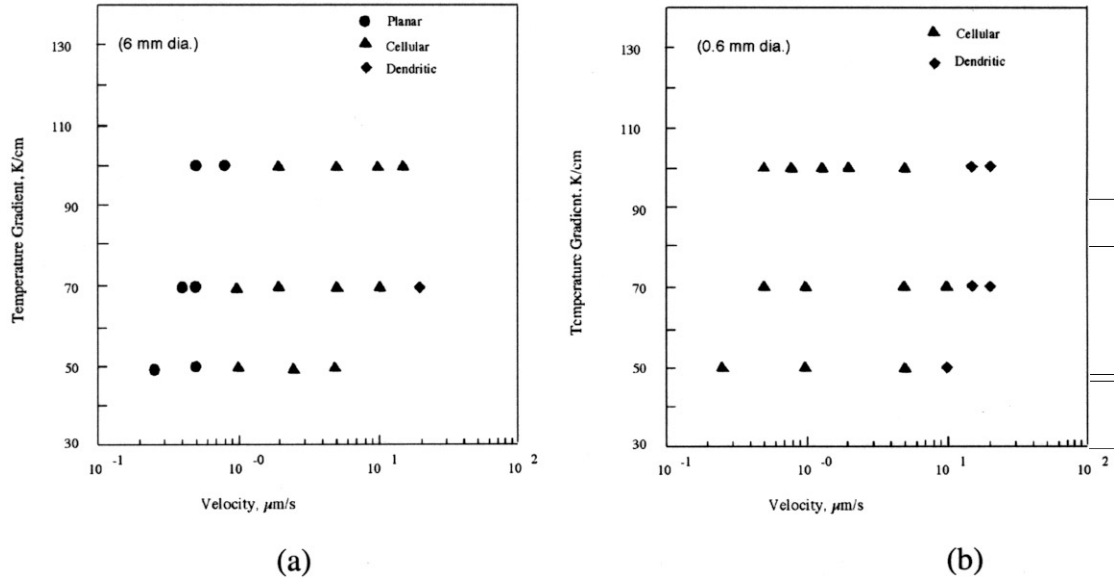


Fig. 4 The interface morphology as a function of temperature gradient G and growth velocity V . (a) $\phi 6.0$ mm sample where significant convection exists. (b) $\phi 0.6$ mm sample in which diffusive growth was present.

4. Determination of ε_d and D_L

4.1 Diffusion coefficient D_L . Solute diffusion coefficient in liquid has been reported by different researchers [12,13,14]. The typical method is to solidify the sample directionally, quench the sample and analyze the concentration boundary layer ahead of the quenched interface. The sample size reported varies from $\phi 2.0$ mm to 6.0mm, and the diffusion coefficient tends to increase with the sample size. This is easy to understand since liquid convection present in large samples will enhance the solute transport. This connective part has long been ignored in the previous research and consequently the derived diffusion coefficient was not the intrinsic one.

In the present study, it has been verified that growth in a sample $< \phi 1.0$ mm is diffusive, so similar technique has been adopted to determine the composition profile ahead of the quenched interface. Figure 5 shows the microprobe analysis of the solute composition in the sample for both a thin and a bulk sample prepared under the sample condition (G, V, C_o, f_s). Obviously, the thin sample has a higher composition in both solid and liquid side.

It should be pointed out that the solid composition at the interface is ~ 2.33 wt%Cu, much less than the alloy composition (4.0wt%Cu), the growth was still in the initial transient regime. The concentration boundary layer was still building up and the interface velocity was consequently lower than the external pulling velocity.

Flux balance at the growing interface is used to calculate the diffusion coefficient:

$$-D_L \frac{\partial C_{Li}}{\partial z} = V_i C_{Li} (1 - k)$$

C_{Li} is the interface composition in the liquid and was measured (Fig. 5). By fitting the composition profile in the liquid, the composition gradient term can also be obtained. The instant interface velocity, V_i , remains unknown in the initial transient. Warren-Langer model about the initial transient [16] has been applied to compute the V_i and it is found that when the solid composition reaches 2.33wt%Cu, the instant interface

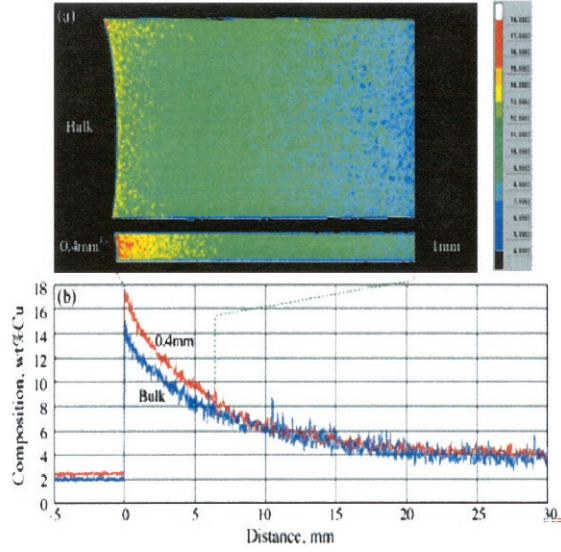


Fig. 5 Composition profile in a $\phi 6.0\text{mm}$ sample and a $\phi 0.4\text{mm}$ thin sample. Note the difference in composition in the solid and the concentration boundary layer in the liquid.

velocity is $0.37\mu\text{m/s}$. Considering that the pulling velocity is $0.4\mu\text{m/s}$, the interface velocity is only 7.5% lower than the steady state planar interface velocity.

With $\partial C_{Li}/\partial z$, C_{Li} , V_i , and k known, the intrinsic diffusion coefficient is found to be $2.4 \times 10^{-9} \text{ m}^2/\text{s}$. This is significantly smaller than those reported values since the thin sample does not have liquid flow inside.

4.2 Anisotropy in interfacial energy ϵ_4 . The influence of anisotropic interfacial properties has emerged as a critical issue with regard to morphological evolution and the selection of relevant length scales in solidification microstructures. Although the importance of interface energy anisotropy is well recognized, reported measurements are limited and the magnitude of anisotropy is not well established for metallic alloys. We have developed an experimental technique to accurately obtain this parameter.

The principle of the technique is based on Wulff theorem. A negative crystal or a droplet embedded in a matrix has been used successfully to obtain the ϵ_4 for a few transparent materials (see ref. [17] for a complete list of the materials ever reported), however the same method has not been successfully used for opaque metallic samples due to the experimental difficulties involved [18].

A typical droplet is shown in Fig. 6. The observation is in a (001) plane and the droplet in this plane has a four-fold symmetry, which is shown nicely for the droplet in Fig. 6. We overlapped two circles on this droplet: one is tangential to the $\langle 110 \rangle$ direction and the other is tangential to $\langle 001 \rangle$ direction. In the solid matrix, the composition is rather uniform, while in the quenched liquid side, the composition quickly jumps, and the ratio of the solid composition over the average liquid composition is ~ 0.16 , in agreement with the phase diagram. Figure 7 shows the result of the measurements conducted on 28 droplets and the average value based on the statistical analysis of these data is 0.0097 ± 0.0008 . This is the first reported anisotropy in an opaque metal with small anisotropy.

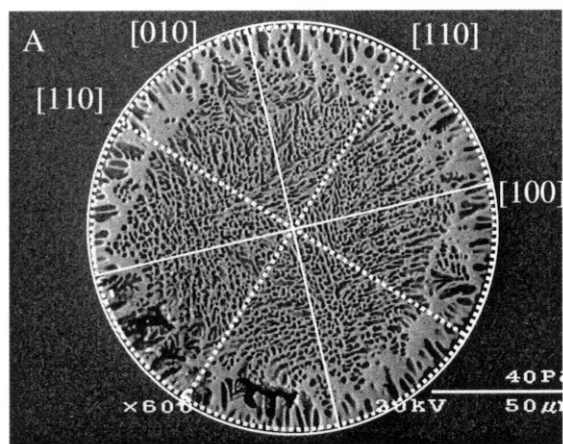


Fig. 6 Equilibrium shapes of the droplet “A”, observed on diametrical cross-sections normal to a <001> direction in the continuous phase.

5. Evaluation of quenching effect

The metallic samples need to be quenched for metallurgical observation/analysis. Interface is supposed to be moving a short distance in this quenching operation but no quantitative study has been made about how much the interface will move. This is a crucial problem in analyzing the patterns formed in the solidification.

An experimental method has been devised to quantify the interface advance in the quenching process. Figure 8(a) shows one sample in our analysis. The sample was kept stationary so the interface was flat in the region of interest and the composition in the solid is uniform. Then the sample was quickly dropped into the quenchant (liquid Sn-Ga-In eutectic alloy). The interface would move some distance before it destabilized and evolved into fine dendrite structure. In this moving process, the interface composition quickly increased and can be obtained by SEM/Microprobe analysis. The distance between the uniform composition and the destabilized interface should be the interface advance during the quenching (δ in Fig. 8(a)). Different quenching rates were adopted and Fig. 8 (b) shows the result for five different quenching rates. The higher the quenching rate, the smaller the interface advance. However further increase in the quenching rate beyond 100 K/s does not significantly reduce δ value any more. This is believed to be limited by the poor thermal properties of the alumina ampoule used in the study.

In this research project, it is critical to determine the shape of the cell/dendrite tip in the post-flight analysis. Therefore more experiments were conducted to determine if the cellular interface shape would distort during quenching. Figure 9 was one such an example. Similar composition measurement was made and the original interface shape prior to quenching was recovered from the composition profiles (dashed line in the figure). It is found that quenching caused all the points on the interface to move nearly the same distance before the interface destabilized. Therefore the quenched interface marked by the θ phase after quench can still represent the original shape of the cell/dendrite before quenching.

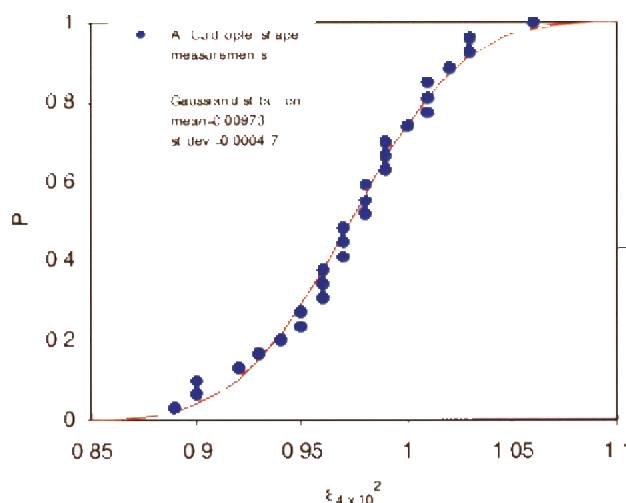


Fig. 7 Distribution of the measured anisotropy for Al-4.0wt%Cu. It is of Gaussian type and gives the mean value of 0.0098

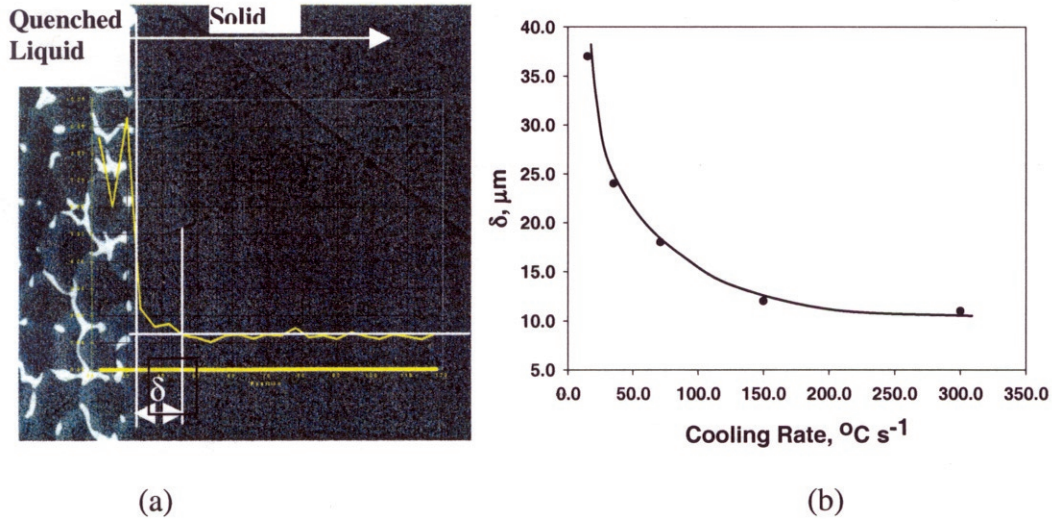


Fig. 8 (a) A quenched Al-4.0wt%Cu sample superimposed with measured composition profile, indicating the composition jump with the quench operation and the definition of interface advance parameter δ .
 (b) The variation of δ with quench rate.

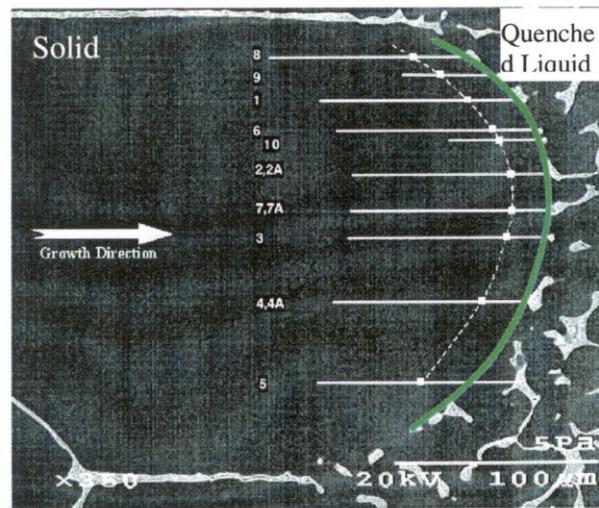


Fig. 9 Solid/liquid interface advance with the quenching operation. Interface points moved nearly parallel except those points very close to the cell boundary, therefore the quenched shaped indicated by the green line should still represent the original shape before quenching

6. Determination of transient distance for cellular structures

The transient distance for cellular structures is crucial in this research since the cell shape will be reconstructed through serial micro-milling. A systematic experimental study has been carried out to determine this transient distance by three different techniques: Minimum Spanning Tree (MST), statistical analysis of primary spacing and Voronoi polygon construction based on the mass center [20]. The first two are to judge the spacing distribution and the latter is to determine the cell arrangement.

A series of samples was directionally solidified at 10 μm/s and 11.0K/mm but quenched after growing different distances (different solid fraction). The growth distance was 3, 6, 9 and 12 cm long respectively and the growth morphology was all deep cells. Figure 10 shows the Voronoi polygon analysis for the sections with 3cm (Fig. 10(a)) and 9 cm (Fig. 10(b)) growth length and clearly they are of almost the

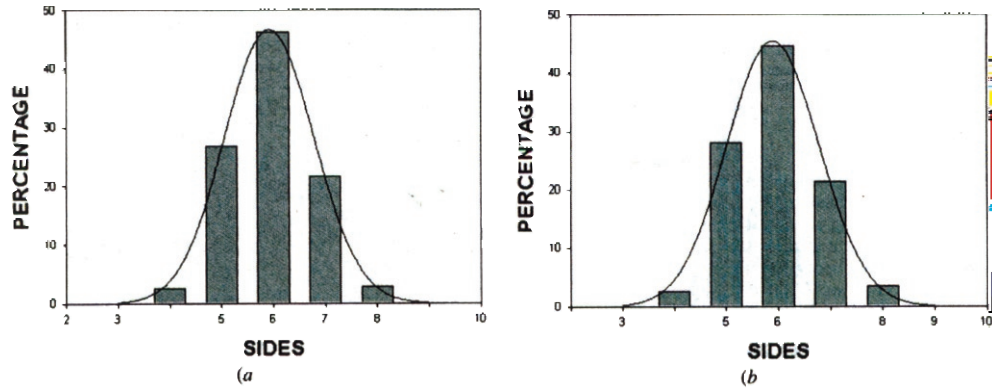


Fig. 10 Frequency distribution of the number of nearest neighbors in directionally solidified Al-Cu alloy deep cells. (a) solidified 3 cm before quenching, (b) solidified 9 cm before quenching

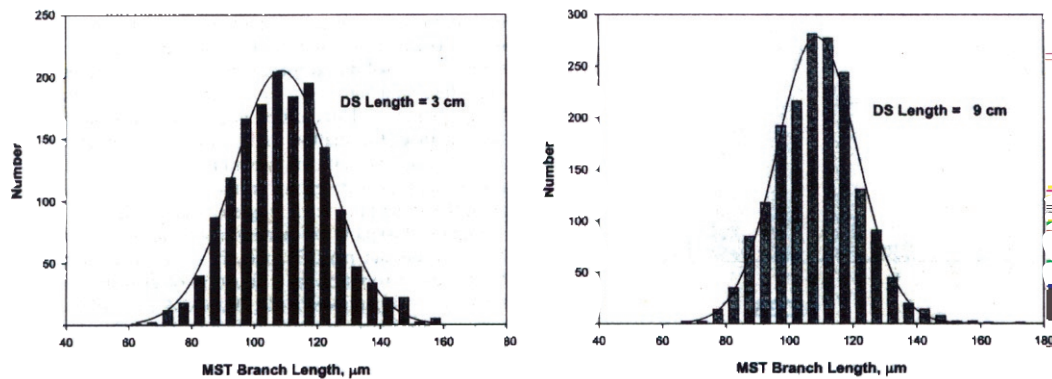


Fig. 11 MST obtained from the cell center images for two Al-4.1wt%Cu alloys.

Left: Directionally solidify 3cm before quenching

Right: Directionally solidify 9 cm before quenching

same distribution for the number of nearest neighbors and highest percentage corresponds to hexagonally arranged cells. Figure 11 shows the MST results for 3cm (Fig. 11(a)) and 9cm (Fig. 11(b)) growth length. Once again, they appear to have the same MST frequency distribution. The mean branch length is $109.3 \pm 15.5 \mu\text{m}$ and $109.0 \pm 13.2 \mu\text{m}$ respectively, implying the average primary spacing and the spacing distribution are identical within the measurement error. This result indicates that transient length for spacing distribution is no more than 3cm. The mushy zone length for Al-4.1wt%Cu to grow at 11.0 K/mm and $10 \mu\text{m/s}$ is $\sim 1 \text{ cm}$, therefore the overall steady state primary arm spacing distribution is achieved when the sample solidifies about three mushy zone lengths.

Microgravity relevance

This research project concentrates on physics of the cell/dendrite transition in the directional solidification process, therefore cell shapes and cellular array stability constitutes the key part of the research. Our numerical modeling and extensive ground-based experiments have ambiguously shown that the cellular growth regime is strongly influenced by melt flow on earth. The thin sample technique can offer a diffusive growth surrounding, but the constraint from the ampoule wall limits the ability to study the array stability of cellular structure. The ideal configuration for cellular structures is the controlled diffusive solidification in a bulk sample ($> 3.0 \text{ mm}$), which facilitates the utilization of microgravity surroundings.

Conclusion

1. Convection dominates the pattern formation in a bulk sample. The radially varying morphology can be understood by local composition.
2. A full-scale model, developed to disclose the nature of the convection patterns and thermosolutal transport in the bulk melt, predicts that diffusive growth can occur under three conditions: microgravity, capillary sample and/or high growth rate. The effect from sample size and growth rate is clearly verified in the capillary sample growth experiments.
3. Morphologies in the thin sample is significantly different from that in the bulk. Cells may grow in the thin sample but planar front growth is observed in the bulk and dendrites grow in a thin sample while cells grow in the bulk. The seemingly enhanced interface stability is because convection causes macrosegregation in the bulk.
4. Morphological evolution in both convective ($>\phi 3\text{mm}$ sample) and diffusive ($<\phi 1\text{mm}$ sample) has been thoroughly investigated and convection is found to stabilize the growth interface.
5. A technique has been developed to measure the anisotropy of the L/S interfacial energy for metallic alloys. This value for Al-4.0wt%Cu is 0.0098.
6. A strategy has been developed to precisely obtain the intrinsic solute diffusion coefficient in liquid. The value evaluated from a diffusive directional solidification process is $2.4 \times 10^{-9} \text{ m}^2/\text{s}$, significantly smaller than the reported value obtained in a bulk sample.
7. S/L interface is found to advance during the quenching process. An experimental technique was devised to characterize this parameter that decreases with the enhanced quench. For cell and dendrite tips, the interface points advance the same distance within the experimental error, thus the quenched interface still represents the original L/S interface prior to quenching.
8. The transient process for the cellular structure has been studied with different statistical methods and it is shown that when the growth distance is 3 time longer than the mushy zone length, the cellular array will reach its statistical steady state.
9. All experimental studies in the bulk sample in planar, cellular and low-velocity dendritic growth are influenced by convection and should not compare with the diffusive growth model directly. Thin sample growth technique developed here can get diffusive growth terrestrially but the confined space limits the possibility to study array stability. It inevitably needs the microgravity surroundings to study the cellular growth and cell/dendrite transitions in solidification process.

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SMALL PARTICLE RESPONSE TO FLUID MOTION USING TETHERED PARTICLES TO SIMULATE MICROGRAVITY

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Abstract

This paper reports on ground based work conducted to support the Spaceflight Definition project SHIVA (Spaceflight Holography Investigation in a Virtual Apparatus). SHIVA will advance our understanding of the movement of a particle in a fluid. Gravity usually dominates the equations of motion, but in microgravity as well as on earth other terms can become important. Through an innovative application of fractional differential equations, two members of our team produced the first analytical solution of a fundamental equation of motion, which had only been solved numerically or by approximation before. The general solution predicts that the usually neglected history term becomes important in particle response to a sinusoidal fluid movement when the characteristic viscous time is in the same order as the fluid oscillation period and peaks when the two times are equal. In this case three force terms, the Stokes drag, the added mass, and the history drag must all be included in predicting particle movement. We have developed diagnostic recording methods using holography to save all of the particle field data, allowing the experiment to essentially be transferred from space back to earth in what we call the “virtual apparatus” for on-earth microgravity experimentation. We can quantify precisely the three-dimensional motion of sets of particles, allowing us to test and apply the new analytical solutions.

We are examining the response of particles up to 2 mm radius to fluid oscillation at frequencies up to 80 Hz with amplitudes up to 200 microns. Ground studies to support the flight development program have employed various schemes to simulate microgravity. One of the most reliable and meaningful methods uses spheres tethered to a fine hair suspended in the fluid. We have also investigated particles with nearly neutral buoyancy. Recordings are made at the peak amplitudes of vibration of the cell providing a measure of the ratio of fluid to particle amplitude. The experiment requires precise location of the particle to within microns during recording, and techniques for achieving this are one of the project challenges. Focused microscopic images and diffraction patterns are used. To make the experiment more versatile, the spaceflight system will record holograms both on film and electronically. A cross correlation procedure enables sub pixel accuracies for electronic recordings, partially accommodating the lower spatial resolution of CCDs. The electronic holograms can be down linked providing real time data. Results of the ground experiments, the flight experiment design, and data analysis procedures are reported.

Keywords: particle dynamics, Stokes flow, microgravity, holography

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Ground Experiment Objectives and Strategy

Our analytical solution to the particle/fluid equation of motion¹ was used to design both ground and flight experiments that will experimentally test cases that are significantly different from previously approximations and numerical solutions. Our solution shows that the history term cannot be neglected for many interesting cases (especially low Reynolds number cases). A fundamental case that has been selected for study is that of a particle suspended in a fluid that is oscillating sinusoidally. Since the movement of a particle in response to the surrounding fluid is predicted by our solutions, we can test the theory by measuring that response, specifically, the ratio of the particle to fluid amplitude, η and their phase relationship.

The problems of conducting the experiments on earth include particles rising or falling too fast violating the low Reynolds number assumption and the difficulty in locating the particle position with great accuracy when the particle is rising or falling. In a gravitational field as the fluid to particle density ratio, α , approaches unity, the rate of rising or sinking of the particle is small, a precise measurement of particle position is easy to make, and the Reynolds number is small. However, to study the history drag as α approaches unity requires better measurement accuracy because η also approaches unity. Our ground investigation has addressed this in various ways, but the most versatile so far has been a tethered particle method. Particles are tethered on a fiber that holds them in the proper position for recording. This simulates microgravity better, gives much more time, and simplifies recording at the expense of the interference of the tethering fiber. We found this method very effective, although effects from the tethering fiber are observed. The tethering method was used for much of the ground science work.

We have proven in ground experiments that we can locate a particle in a vibrating test cell with a precision sufficient to measure the effect of the history term on the particle amplitude. A specific case that has been tested extensively at MetroLaser is a 1mm-radius polypropylene particle in a Krytox liquid filled cell that is shaken at frequencies up to 100 Hz with amplitude of up to 0.2 mm. The required precision ranges from about 5 microns or better depending on the amplitude of vibration and the value of α . We have run many experiments around the region where the scaling function $S = 1$ (S is the ratio of viscous time to vibration period, and at S equals unity the motion information transfers about one particle diameter during one cycle of oscillation) and with $\alpha = 2.1$. The effect of the history term peaks at about 60 Hz for this case making this an optimum frequency for observing the history term effects. A vibrational amplitude of 100 microns should result in a 15-micron difference with and without the history term. We have shown in our ground experiments that we are at least a factor of two better than the resolution required to quantify the effect.

The objectives of the ground experiments are:

- Establish that the measurement accuracy and resolution required to achieve our project goals are achievable.
- Prove that the flight experiment is feasible with attainable hardware.
- Evaluate the capability of critical hardware components to meet experiment requirements (e.g. laser power and coherence, photographic film properties)
- Support the project science with limited testing of the new solutions to the equations of motion. Test the theory in as wide a range and with as many parameters possible on earth.
- Gain experience and test concepts that will be necessary for conducting a spaceflight experiment.
- Develop data reduction and interpretation methods.
- Identify and resolve critical issues.

Experimental Apparatus Development and Testing^{2,3}

Although the ground experiment is much like the anticipated flight experiment, it has a number of complications that are not expected in microgravity. Figure 1 illustrates the experiment with a free particle rising to the surface.

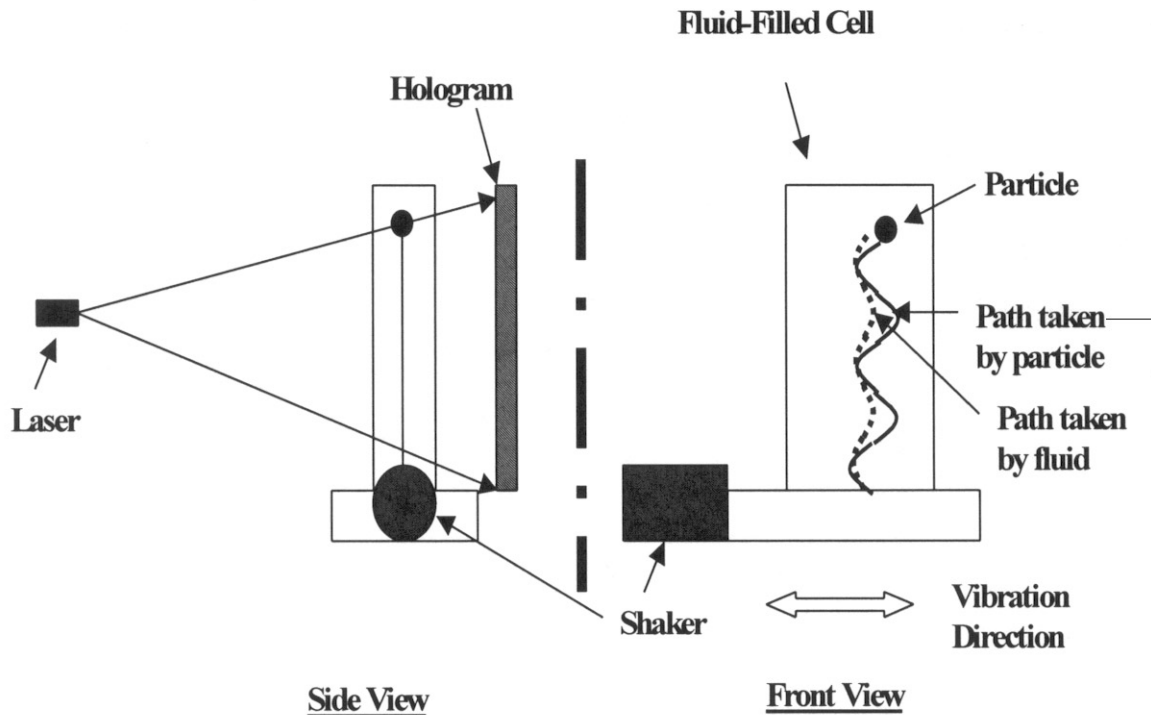


Figure 1. Ground experiment concept.

The problem is to suspend or launch a particle in a fluid filled cell, vibrate the cell along a single axis in a range up to 100 Hz with amplitudes up to ± 200 microns and locate the positions of both the cell and the particle at two different times with micron precision. The cell must be completely filled with fluid at all times during the measurement phase. Particles rise and fall in the fluid under buoyant forces, so there is not much time for observing a free-floating particle. In Figure 1 the particle is released at the bottom of a fluid filled cell, and the fluid is constrained to move with the cell. Therefore, we can measure precisely where the fluid is at all times. As the particle rises, it attempts to follow the sinusoidal movement of the fluid; however, it follows a quasi-sinusoidal path with some phase difference and larger amplitude (see particle and fluid motion in the figure). Our early experiments were done with particles as shown in the figure. The cell design and the particle suspending procedure passed through many evolutions before we arrived at a reliable repeatable experimental apparatus that employed the tethered particle.

Figure 2 shows the ground experimental apparatus. To achieve the required precision and to maintain a single vibration axis it was necessary to mount the cell on a single axis traverse. Tuning and stiffening the apparatus resolved vibrational noise and resonance issues. Removing errors caused by optical system vibration presented a major challenge at the required accuracy. The most reliable choice for a vibrational source was a commercially available electromagnetic shaker (voice coil) that had been selected by the NASA engineering team as a strong candidate for the flight system. It was shown to be entirely effective for the experiment and was eventually adopted as the preferred method for the ground science as well. The

cell holds an approximately four-centimeter cube of fluid between two windows. It provides the ability to test the interaction of particles with the walls and with each other. The cell was designed so that a wall could be moved closer and closer to the particle to evaluate wall effects. In addition, the design allows multiple particles to be tethered and observed.

The system reliably produces vibrational conditions from 30 to 80 Hertz with amplitudes up to 150 microns. So far we have used tethered polypropylene, steel and magnesium, 1 mm radius spheres. We ran a number of tests to determine phase difference in the particle and cell both to measure the effect on our accuracy and also to test the predictions of the theory. We were able to measure the particle phase lead and compared this with theory. The results are within reasonable agreement with the theory.

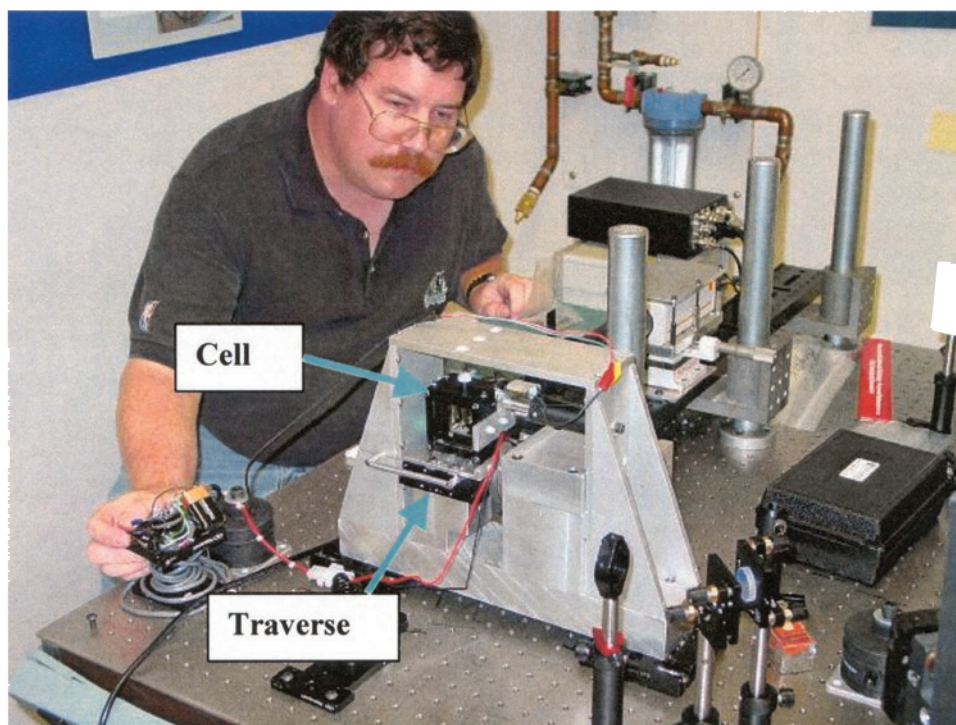


Figure 2 a). Overall view of the ground experiment.

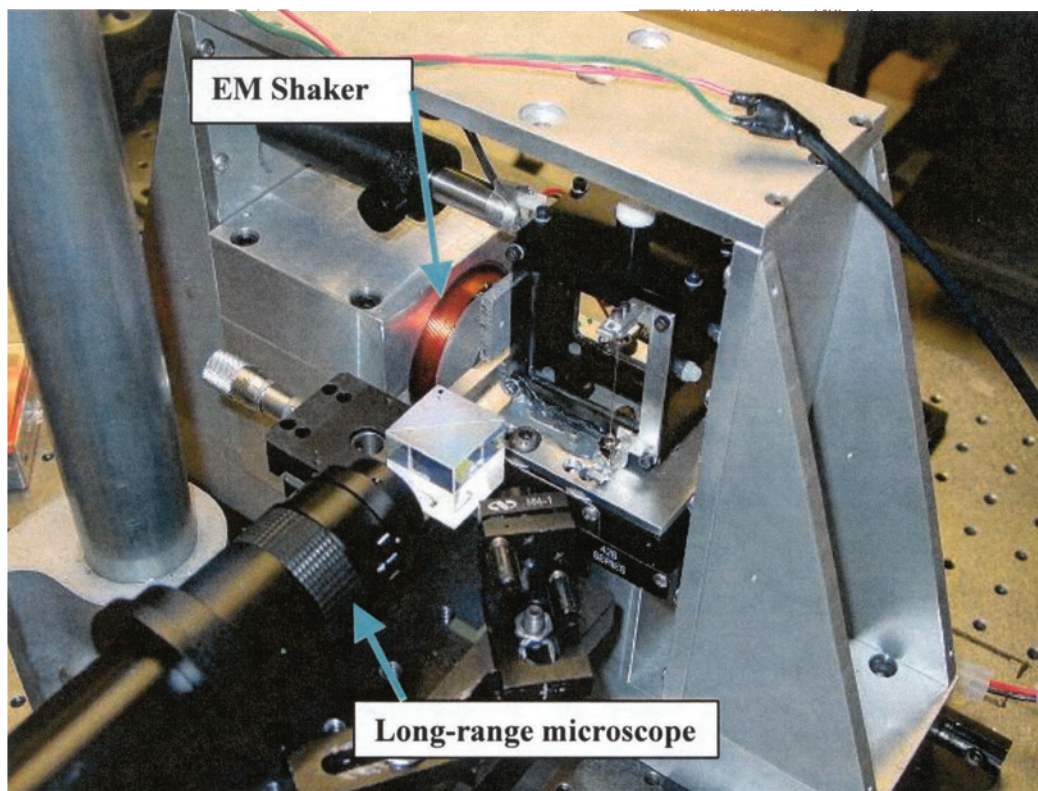


Figure 2 b). Ground cell from long range microscope side.

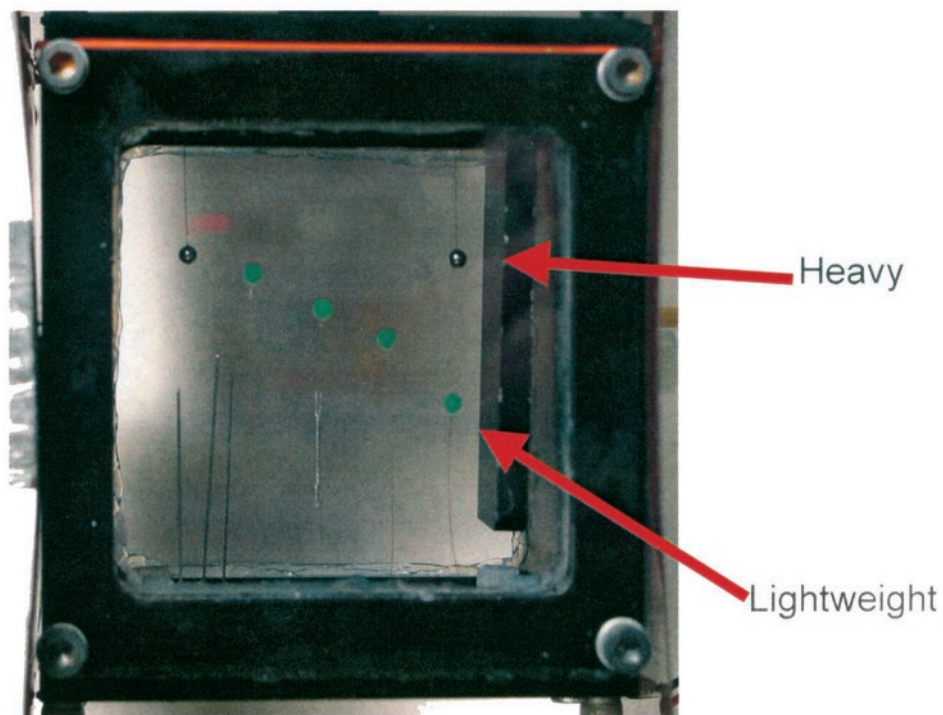


Figure 2 c). Cell showing tethered polypropylene and steel particles (note particles near the wall).

Figure 2. Ground experiment apparatus.

Determining the Ratio of Particle to Fluid Amplitude

To determine the ratio of the particle to fluid amplitude requires that the fluid and particle positions be determined at least at two times in the cycle of vibration. Two measurement methods have been adopted:

1. In the same recording, record two positions of the particle and a reference point on the cell, preferably when the cell positions are at its extremes. This will allow us to make an accurate measurement of the fluid to particle amplitude. The fluid, being confined by the cell, will move by the same amount as the cell. The exposures must be short enough so that the particle does not move more than a few microns during the exposure. This will be most easily achieved at the maximum amplitude where the velocity of the particle and cell are at zero. In addition, at this condition the dimension, being at its greatest value, can be measured more accurately. It should be noted that the phase difference between the fluid and the particle is small enough for most cases to be neglected in making the amplitude measurements; however not in all cases. It must be accounted for in some cases.
2. In two different recordings, record the two positions of the particle and a reference point on the cell as in the first method. Registration is required between the two different recordings to make measurements of changes that took place in the time between the recordings.

The particle and cell positions or amplitudes must be determined with an accuracy of 5 microns. It would be beneficial to do better than this, say one to two microns. The particle and cell positions can be determined by locating edges or centroids.

Locating the edge of a focused microscopic image produced by the hologram with the required accuracy is a relatively straightforward procedure; however, with electronic (CCD) images, the problem is different. Typically, the 10 microns pixels are the limiting factor, and sub pixel resolution requires additional image handling and processing. Sub pixel imaging is more easily achieved on a distributed light pattern such as an out of focus image or a diffraction pattern. Figure 3 shows a diffraction pattern of a 1 mm radius magnesium sphere suspended in Krytox. By performing a cross correlation between two recordings of this pattern, which is distributed over many pixels, the center of the Poisson's pattern can be located to a small fraction of a pixel. We found that the portion of the diffraction pattern in the shadow of the particle that contains the Poisson's spot, shown in the top right of the photo, provides an excellent noise free, predictable light pattern (shown in the bottom right) that can be used as a correlation template with both single and double exposure recordings. The correlation templated is then cross-correlated with the single or double exposures, giving a correlation peak at the center of each diffraction pattern in the recording.

Figure 4 shows an actual correlation peak produced by correlating a template produced from the diffraction pattern with the diffraction pattern, showing the center position location through interpolation to better than 0.1 pixels.

The Tethered Particle Method

A fiber was attached to the particle, which is then held in the center of the cell, by attaching the other end of the hair to the bottom of the cell (or the top for heavy particles). This method proved useful especially for large particles.

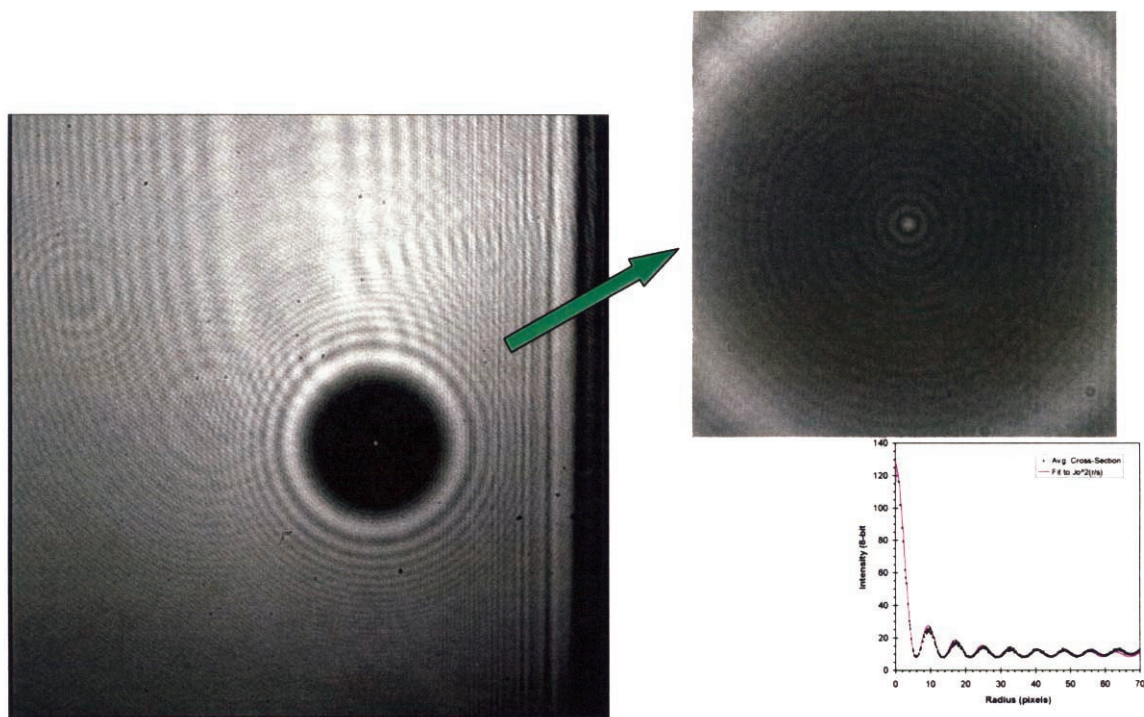


Figure 3. Fresnel Diffraction Pattern of a 1 mm Radius Sphere, showing the Poisson's spot and pattern and theoretical intensity distribution.

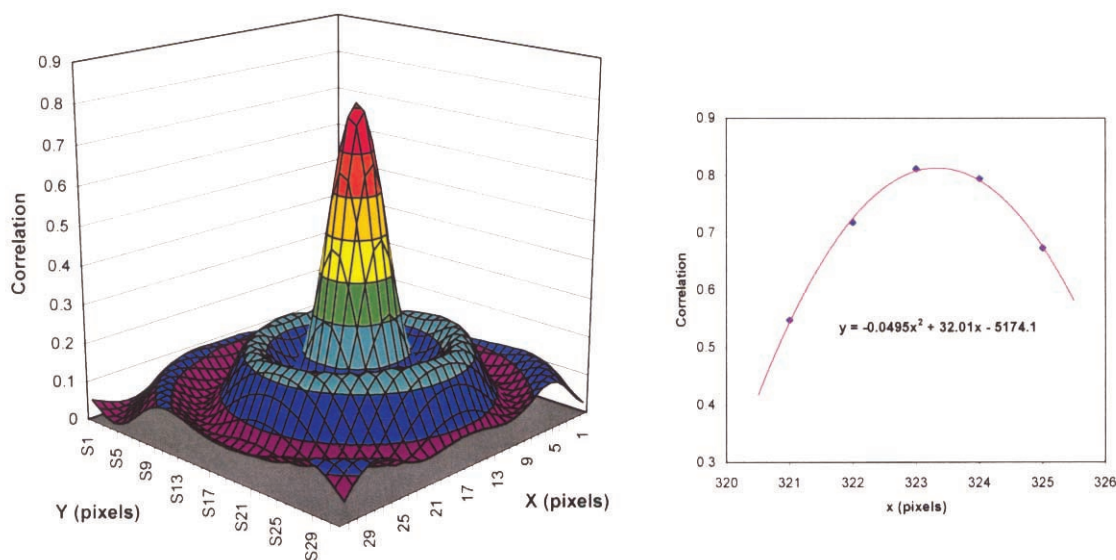


Figure 4. Cross-correlation of a template with the diffraction pattern in Figure 3. The curve on the right hand side shows that the center of the correlation can be located through interpolation with sub pixel accuracy.

Figure 5 shows a tethered 1 mm radius polypropylene particle tethered on a 100-micron diameter fiber. In this figure, the holograms are recorded at two times, when the sphere is located at extremes of the vibration. With this configuration, we have been able to examine many different types of particles, particle interactions, and particle wall interactions.

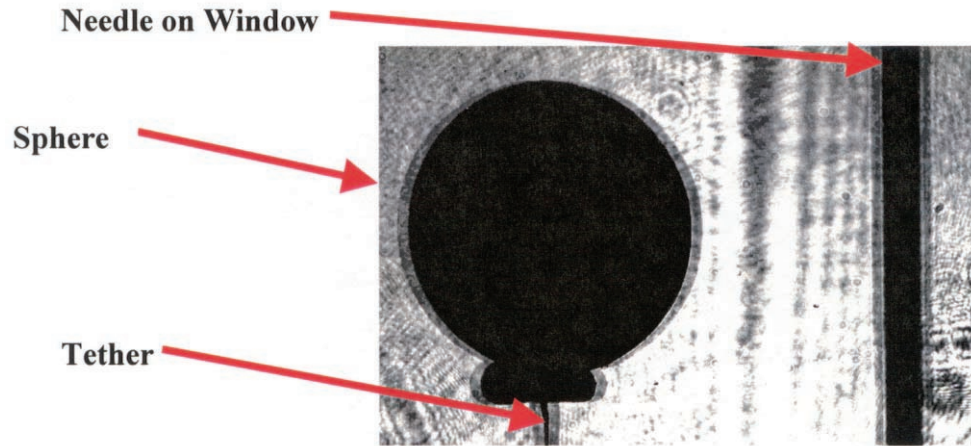


Figure 5. A 1 mm tethered sphere undergoing vibration.

Figure 6 shows a plot of the amplitude of particle motion to fluid motion at various amplitudes for a free particle. The slope of this line provides the predicted parameter, η . By taking several points on the curve to produce this value, the accuracy can be improved considerably to even better than what would be provided with the best position accuracy at a single point. The predicted value in these cases was within 1% of the measured value.

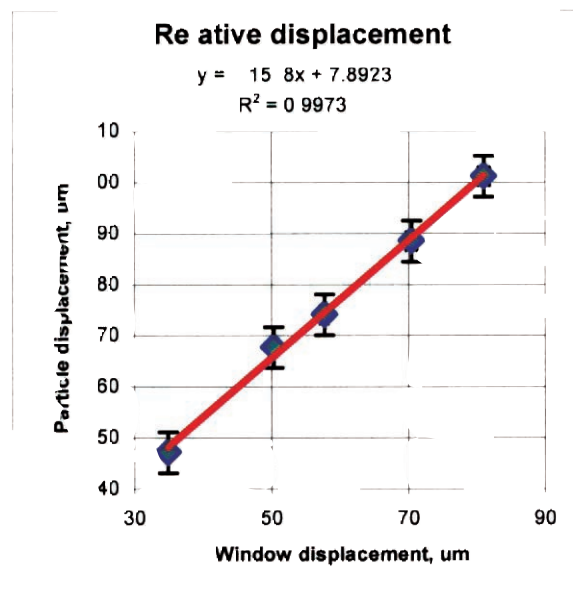


Figure 6. Ratio of particle to fluid displacement at 60 Hz vibration. The important number is the slope, or 1.1518. This number falls within 1% of the value predicted by the Coimbra-Rangel solution. The parameter $S=1$, and $\alpha=2$.

We took data for a range of vibration amplitudes over a frequency range from 30 to 80 Hz. for a tethered 1mm radius sphere. Figure 7 shows a frequency sweep at three different amplitudes of a tethered 1mm radius sphere. Note that the ratios are significantly smaller than the case of the free particle, suggesting the effect of the tether on the particle motion is not negligible for this case.

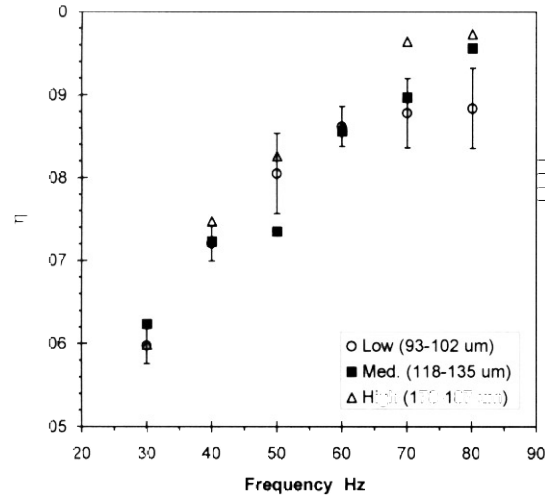


Figure 7. Plot of ratio $\eta = A_p/A_c$ vs. cell oscillation frequency for polypropylene particle in krytox ($\alpha=1.1$). The particle was located near the center of the cell, and did not interact with the walls. Three different data sets are shown for three A_c ranges: low amplitude ($A_c = 93\text{-}102\ \mu\text{m}$), medium amplitude ($A_c=118\text{-}135\ \mu\text{m}$), and high amplitude ($A_c=178\text{-}187\ \mu\text{m}$). Uncertainty bars for η are plotted for the low amplitude data set. The uncertainty in the frequency is typically 0.2 Hz.

Experiments include particles interacting with walls and other particles. Figure 8 shows the results of an experiment designed to examine the effect interaction between the cell wall and the particle. In this experiment, the center of the polypropylene particle was 5.2 mm away from the wall. At each frequency, the ratio η was greater for the wall-interacting particle than for the non-interacting particle, an unexpected result.

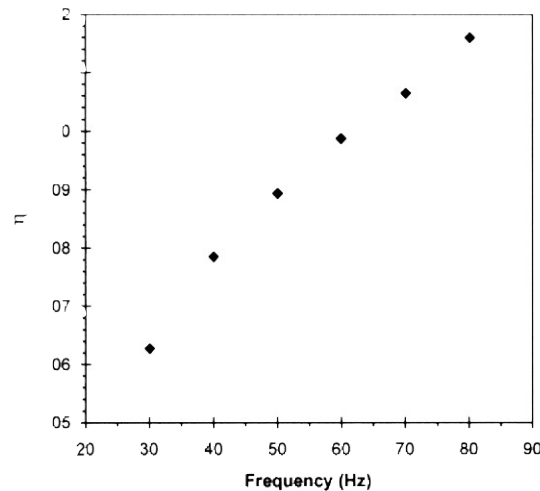


Figure 8. Plot of ratio $\eta = A_p/A_c$ vs. cell oscillation frequency for a polypropylene particle in krytox ($\alpha=2.1$) whose center is 5.2 mm from a wall. A_c ranged from 125 to 142 microns. For a given frequency, η is higher for the wall-interacting particle than for the non-interacting particle. The uncertainties in η and frequency are approximately the same as those in figure 3. Each point represents the average of 10 separate measurements.

Figure 9 shows the results of an experiment designed to examine the effect of oscillation frequency on the motion of a steel particle in krytox ($\alpha=.24$). Because steel is denser than krytox, the particle displacement is always less than the cell displacement. As the frequency increases, η decreases.

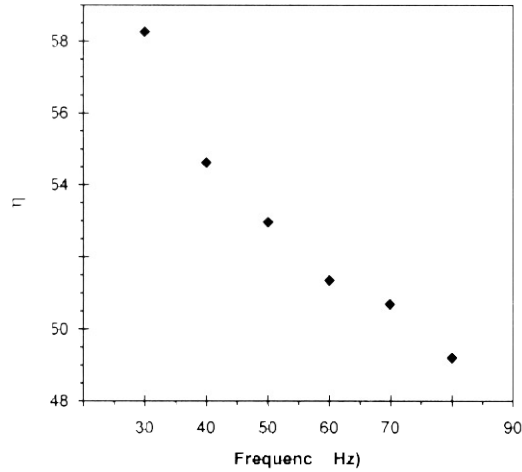


Figure 9. Plot of ratio $\eta = A_p/A_c$ vs. cell oscillation frequency for a steel particle in krytox ($\alpha=.24$). The particle was located near the center of the cell, and did not interact with the walls. A_c ranged from 138 to 149 μm .

Figure 10 shows a plot of η versus frequency for a magnesium alloy particle in krytox ($\alpha = 1.10$). The theory predicts that η should be slightly greater than 1 for this particle, however, we observe the surprising result that all values of η are less than 1. The discrepancy may be due to the drag created by the tether, which would slow the particle and reduce A_p . The effect of tether drag on particles is strongest for particles whose density matches that of the fluid. We will conduct some free particle experiments to confirm this result.

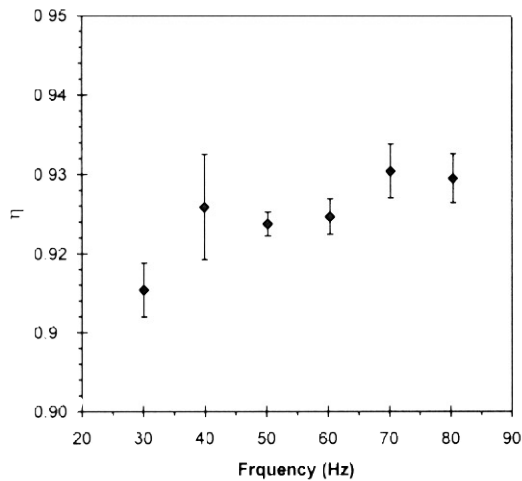


Figure 10. Plot of ratio $\eta = A_p/A_c$ vs. cell oscillation frequency for a magnesium alloy particle in krytox ($\alpha=1.10$). The particle was located near the center of the cell, and did not interact with the walls. A_c ranged from 116 to 138 μm . Uncertainty bars for η are plotted.

The theory predicts that the particle and cell are slightly out of phase, and that a particle with $\alpha = 2$ will reach its extreme of motion a fraction of a millisecond before the cell does. To pinpoint the extremes of particle motion, a series of recordings were made where the first illumination pulse coincided with one extreme of the cell motion, and the delay between the first and second pulses was varied. Figure 11 shows a plot of A_c and A_p versus the time delay between illumination pulses for a cell oscillating at 60.0 Hz. The maximum cell displacement is observed when the time delay is 8.3 ms, which corresponds to one half the oscillation period. The maximum particle displacement is observed at a time delay of 8.0 ms, or 0.3 ms earlier than the cell, which corresponds to a phase difference of 7 ± 2 degrees.

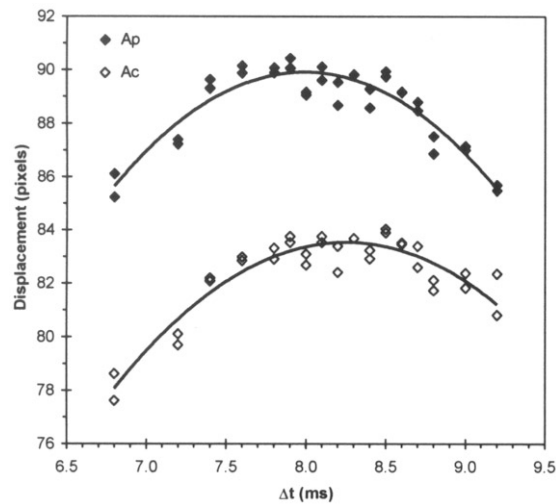


Figure 11. Plots of A_p (black diamonds) and A_c (white diamonds) versus the time between light pulses (Δt) for a polypropylene particle in krytox ($\alpha=0.48$). The cell oscillation frequency was 60.0 ± 0.1 Hz. Each plot is fit by a quadratic polynomial ($A = a\Delta t^2 + b\Delta t + c$). The largest cell displacement is observed when $\Delta t=8.3$ ms, while the largest particle displacement is observed when $\Delta t=8.0$ ms. The uncertainty in the displacements is approximately 1 pixel, which corresponds to $1.8 \mu\text{m}$.

Conclusions

In the foregoing, we have presented some results of a ground based experimental program that is designed to support the flight experiment SHIVA. We have proven that we can determine the position of a particle and fluid with sufficient accuracy to test the analytical solutions of the general equations of motion of a particle in a fluid. We have verified the solutions for a limited range of experimental parameters that can be met on earth. We have used a tethered particle method to simulate microgravity in the conduct of a wider range of parameters. Our preliminary experiments have shown that the tethering fiber does affect particle movement and we continue to search for methods that reduce tether effects.

Acknowledgments

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USE OF ORGANIC STRUCTURE DIRECTING AGENTS TO CONTROL THE MORPHOLOGY OF ZEOLITE CRYSTALS

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Introduction

Zeolites are crystalline materials with periodic arrangements of cages and channels of nanometer dimensions. Their tailored structure, stability and activity have led to a broad variety of applications in industry as molecular sieves (e.g., gas separation processes), catalysts (e.g. for catalytic cracking in petroleum refining), adsorbents and ion exchangers with high capacities and selectivities. Thus, zeolites are important for the production of fuels, petrochemicals and other products essential to modern societies, in the efficient use of raw materials, in energy efficiency, and in pollution avoidance or abatement. These materials grown as films can be used as membranes that offer novel opportunities for applications as sensitive chemical sensors, and in electronic¹ and thermoelectric² applications. Moreover, molecular sieve membranes can operate continuously in separation processes under high temperature and corrosive environments and can be easily integrated into membrane reactor configurations leading to the development of new processes unattainable with the current reactor technology. However, the preparation of zeolite films and membranes for demanding applications, like membrane reactors and hydrocarbon gas separations, is hindered by the lack of suitable membrane formation processes leading to films with controlled microstructure, and by the limited fundamental understanding of zeolite nucleation and growth mechanisms.

Our research objective focuses on addressing the critical issues of microstructure control in order to develop structure-properties-synthesis relationships for the reproducible fabrication of zeolite membranes. We are also developing models based on the fundamentals of crystal growth, colloidal interactions, and transport phenomena in order to obtain predictive mathematical models that link processing and microstructure with separation performance. Growth rate data and resulting film microstructure from growth in microgravity experiments will be helpful for testing, refining and validating mathematical models for growth, which at this stage of development cannot include gravitational effects due to the poorly understood nature of the crystallizing mixture. In addition, film growth in microgravity will allow clear benchmarking for the practical benefits of the potential for defect elimination when growth takes place in microgravity by comparing the microstructure and the performance in membrane applications for films developed in microgravity with films grown in our lab.

The Importance of Membrane Microstructure

Tsapatsis and coworkers³⁻⁷ have developed the secondary growth technique for synthesizing zeolite films. This processing scheme (Figure 1) consists of making a colloidal suspension of zeolite nanocrystals that is used to deposit a seed layer on a substrate. This is followed by secondary grain growth of the deposited nanocrystals, leading to a continuous oriented film. The elimination of the nucleation step, due

Keywords: silicalite-1, templates, crystal morphology, membranes, zeolites, new research

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to the presence of seed crystals on the support surface, provides improved flexibility for crystal growth, enhanced reproducibility and scalability.

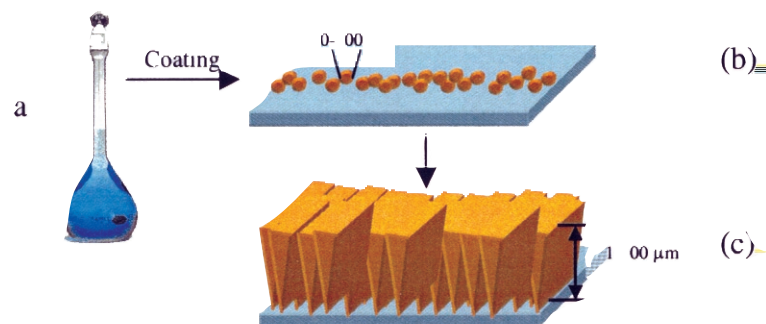


Figure 1. A schematic of the processing scheme for the secondary growth of silicalite-1 membranes.

Panel a shows the colloidal suspension of nanocrystals that is used to coat the substrate shown in panel b. After hydrothermal synthesis, we obtain a continuous film (panel c) due to the growth of the nanocrystals.

Silicalite-1 membranes prepared by this technique exhibit a columnar microstructure (see Figure 1) with a preferred orientation of the crystals within the membrane. One advantage of this growth technique is the ability to manipulate the preferred orientation by adjusting the synthesis temperature. At high temperatures, crystals with c-out-of-plane orientation grow preferentially in the membrane, while at low temperatures $\langle h0h \rangle$ -orientation is observed. In addition to the membrane microstructure, the preferred crystal orientation also influences the surface smoothness and transparency of the membranes. Atomic force microscope pictures of the membrane surface reveal that membranes with a c-out-of-plane orientation have a surface that is rough (Figure 2b), while the $\langle h0h \rangle$ oriented surfaces are much smoother (Figure 2a). This impacts the use of these membranes for optical⁷, photocatalytic or sensor applications.

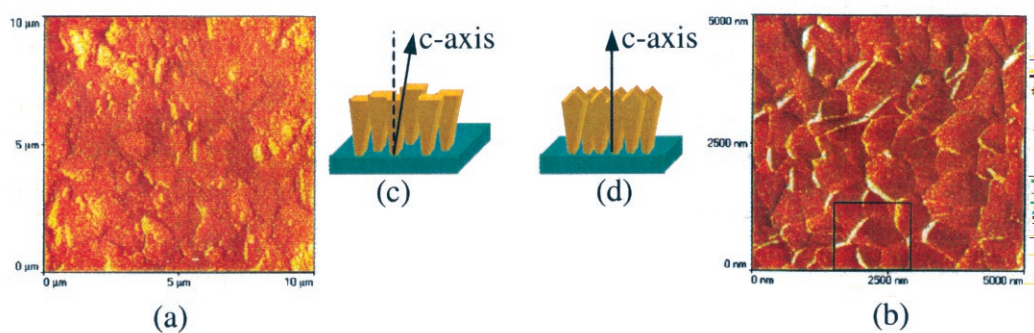


Figure 2. A comparison of the secondary growth synthesis of silicalite-1 membranes (panels a and b) at two different temperatures. An AFM image of the top view of the membrane synthesized at low (high) temperature is shown in panel a (b). Panels c and d show a schematic representation of the $\langle h0h \rangle$ and c-out-of plane oriented membranes, respectively.

One of the characteristics of zeolite crystals is that they exhibit an anisotropic pore structure. In silicalite-1 crystals, sinusoidal channels (a-direction) of circular cross section are interconnected with straight channels (b-direction) of elliptical cross section, while tortuous channels are present along the c-direction. Consequently, in addition to the membrane microstructure, the preferred orientation also has a major impact on the separation characteristics of the membrane. An analysis of the c-oriented membrane microstructure,

using a novel non-destructive tool known as fluorescence confocal optical microscopy (FCOM)⁸, shows a large number of visible grain boundaries throughout the entire thickness of the membrane (Figure 3). However FCOM images from the $\langle h0h \rangle$ oriented membranes show no visible grain boundaries. This implies that the $\langle h0h \rangle$ -oriented membranes have a higher degree of intergrowth than that of the c-oriented membranes. Since both the crystal orientation and grain boundaries play a major role in mass transport through the membrane, we would expect these two membranes to have very different separation characteristics. Studies on the separation of xylene isomers by Xomeritakis et al.⁹ found that the separation factor for the $\langle h0h \rangle$ membranes (Figure 4a) is ~ 30 times higher than that of the c-out-of-plane oriented membranes (Figure 4b).

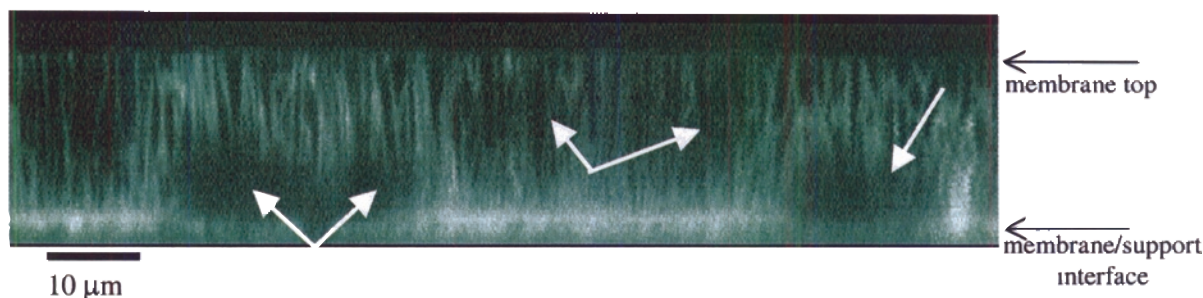


Figure 3. FCOM cross section of a silicalite-1. Grains are columnar structures and are observed throughout the entire thickness of the membrane. The darker areas (arrows) indicate better intergrown sections.

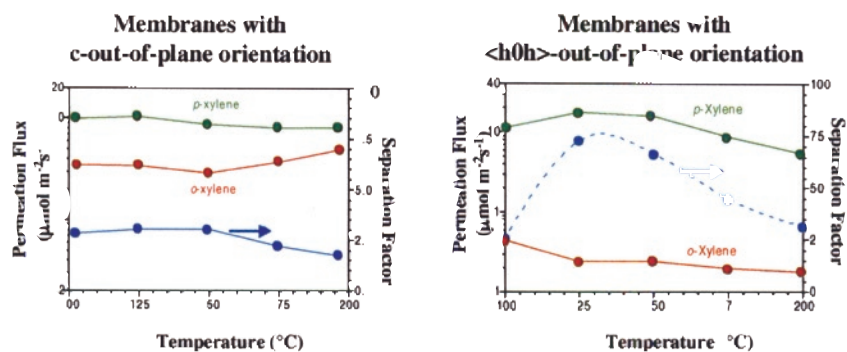


Figure 4. Xylene permeation results for a membrane with (a) $\langle h0h \rangle$ out of plane and (b) c-out of plane preferred orientation.

We have also studied the secondary growth of silicalite-1 crystals in solution and found that the shape of the crystals also varies with the synthesis temperature. At low temperatures, a pill-shaped crystal is observed, with the (h00) faces clearly developed (Figure 5a). However, at high temperatures, the characteristic coffin-shaped crystal is observed, with its (h0l) and (h00) faces clearly developed (Figure 5b). The differences in the crystal shape and in the preferred orientation of the membrane at different synthesis temperatures clearly indicate that the crystal morphology and preferred orientation in the final film are interrelated. Therefore, it is clearly desirable to be able to control the membrane microstructure and orientation through integration of crystal and film growth experiments with computer modeling and simulations.

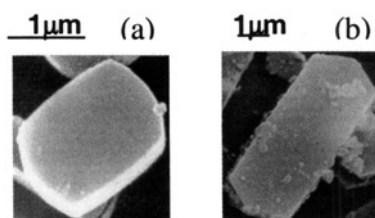


Figure 5. Shape of silicalite-1 crystals subjected to different temperatures.

Multiscale Modeling

Zeolite Nanoparticle Growth Mechanisms

Despite numerous studies on the nucleation and growth of zeolites, their growth mechanism has remained elusive. Aside from oligomers of silica resulting from hydrolysis and condensation reactions of the silica source (e.g., tetraethylorthosilicate), several groups¹⁰⁻¹³ have reported the presence of subcolloidal particles of sizes less than 5 nm during the synthesis of silicalite-1 crystals, using tetrapropylammonium (TPA) as the template or structure-directing agent (SDA). A second population consisting of ~10-15 nm sized units has also been detected by small angle x-ray scattering (SAXS). This population depends on the alkalinity of the solution and results from the aggregation of the smaller subcolloidal particles. Since all these structures contain silica, the primary growth unit driving zeolite growth (Figure 6) has been the subject of debate.

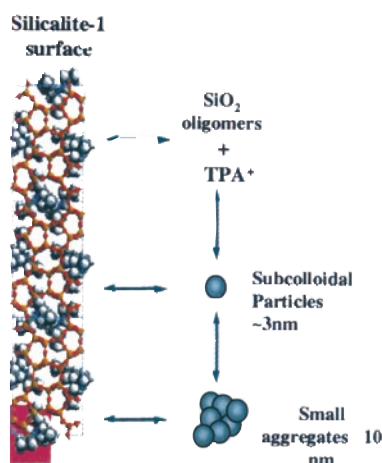


Figure 6. Possible growth units during growth of a silicalite-1 crystal.

Elucidating which are the primary building units for growth of zeolites at the molecular level is critical for tailoring the macroscopic crystal morphology for desired applications. However, this is a formidable task. While small subcolloidal particles have been observed with many experimental techniques, their role in nucleation and growth is still not fully understood. Even their structure/shape is still the subject of intense debate (well-ordered fragments of silicalite-1 vs. amorphous like TPA-silicates), with their role in crystal growth even more debatable (spectator species vs. growth units).

One of our early contributions in this problem is the introduction of mathematical modeling as a tool to screen the consistency of plausible mechanisms. We have developed a fundamentally based growth model for zeolite nanoparticles in the presence of growth units¹⁴. This entails the formulation of a transport equation in terms of the chemical potential. The chemical potential includes contributions from the Brownian motion of growth units as well as the intermolecular forces between growth units

and a silicalite-1 seed. Due to the negatively charged surfaces of zeolites at the high pH of growth, electrostatic interactions play a dominant role at longer distances and van der Waals interactions are important at shorter distances. We have used the DLVO potential to describe intermolecular forces and performed independent experiments (e.g., electrophoresis, atomic force microscopy (AFM), conductivity, and viscosity measurements) to measure various parameters needed for the analysis of dynamic light scattering (DLS) data and parameterization of the DLVO potential. Furthermore, we have performed the first AFM force measurements of a smooth zeolite film as a function of the distance of a small glass sphere attached to an AFM tip. We found that the DLVO potential with constant charge describes the AFM data well and justifies its use in the growth model. The growth model in turn describes the DLS data reasonably well (the only adjustable parameter has been the concentration of growth units) both in terms of growth rate and temperature dependence as seen in Figure 7 (solid lines).

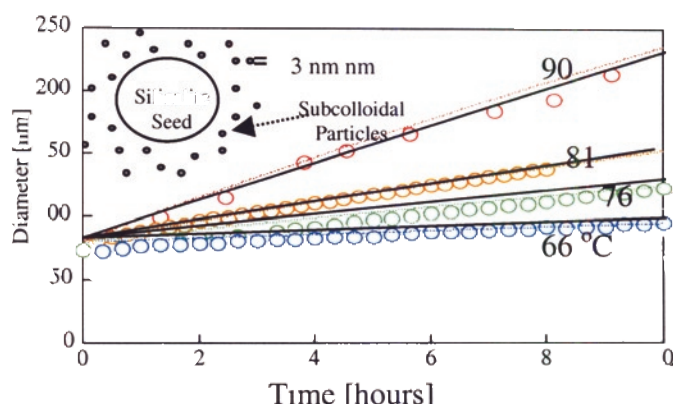


Figure 7. Comparison of experimentally measured (*in situ*) growth curves of MFI seeds by DLS with predicted growth rate of a silicalite particle. The simulation results show the growth of a silicalite particle in a suspension of colloidal nanoparticles considering DLVO and solvation interactions.

This modeling work shows that the only growth unit with the correct activation energy for growth corresponds to the particles with a diameter of approximately 3 nm. This is an important outcome since it provides the first evidence that growth of zeolites proceeds via self-organization of pre-assembled nanoparticles. Such a behavior is in contrast to most typical growth systems where growth proceeds by addition of monomers and possibly dimers. Our combination of DLS data and high resolution TEM (Figure 8) clearly indicate that the measured growth rates of silicalite-1, when TPA is the template, are consistent with a growth mechanism in which the addition of 3 nm subcolloidal particles to the growing crystal is the rate determining step.

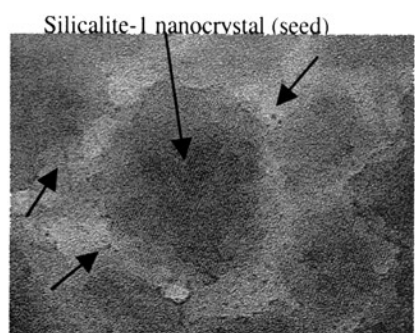


Figure 8. TEM image showing colloidal nanoparticles of 2-3 nm in size (short arrows) in the vicinity of a zeolite crystal.

Development of Preferred Orientation in Membranes

In lieu of in-situ techniques, which are currently not available, mathematical/computational models of the polycrystalline film growth processes are valuable tools for gaining insight into the crystal grain growth processes. In an effort to further understand the microstructural evolution of polycrystalline, faceted MFI films, a simple model was developed to describe the secondary growth process in two spatial dimensions¹⁵. The growth model starts from seeds with initial random orientation and position and is simulated using a marker particle front tracking technique. The model is based on an extension of the “evolutionary selection” theory of film growth proposed by van der Drift over 30 years ago^{16,17}. The simulations clearly illustrate two effects of evolutionary selection: with increasing film thickness (i) a preferential orientation of the crystallites develops and (ii) the average grain size increases. Consequently, the grains become increasingly columnar. Such columnar microstructures, which are common features of polycrystalline MFI films, are due to the competitive growth among adjacent crystal grains. The simulation results are in extremely good qualitative agreement with silicalite-1 membranes grown in our lab (Figure 9).

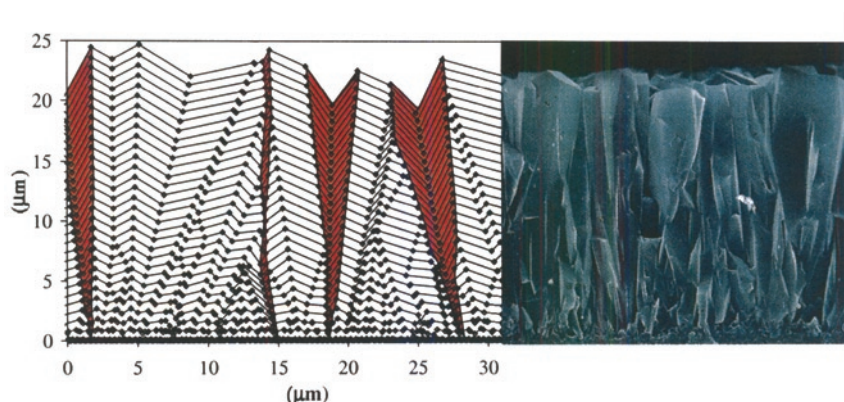


Figure 9. Qualitative comparison of computer simulations of the growth of a silicalite-1 membrane with an SEM image of a silicalite-1 membrane grown by the secondary growth technique.

A key variable that controls the membrane morphology is the ratio of the relative crystal face growth velocities. For example, as this ratio is increased, we observe a significant increase in the surface roughness. The distribution of grains in the final film grown (crystallographic orientation distribution (texture)) was also studied in order to quantify the development of the preferred orientations during vertical growth. This analysis shows two peaks that sharpen during film growth (Figure 10). The first peak position is common to all idiomorphs and may be derived directly from the orientation of the largest radial vector (c-axis) perpendicular to the substrate. The second peak position is dependent on the growth rate parameter and is derived from the orientation of the second largest radial vector in two dimensions. While both peaks had been observed experimentally using X-ray diffraction (XRD) pole figure measurements, the mechanisms that give rise to their existence were not well understood until now. The modeling and simulation studies clearly show that the crystal morphology and the relative growth rates of the crystal faces present have a great influence on the final microstructure of the membrane.

Controlling the Membrane Microstructure

Secondary growth synthesis of silicalite-1 membranes can yield two types of preferred orientation: the crystals are preferentially oriented with either their c-axis or $\langle h0h \rangle$ -axis nearly perpendicular to the substrate. While separations have been demonstrated for both these types of membranes^{9,18}, the observed fluxes are about an order of magnitude too low for commercial use. A desirable configuration for a selective

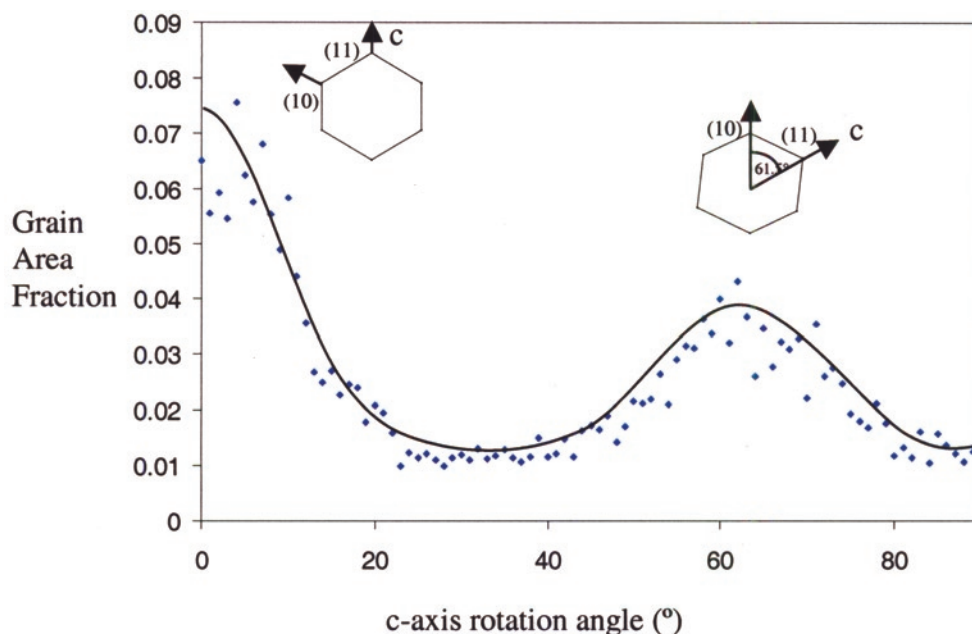
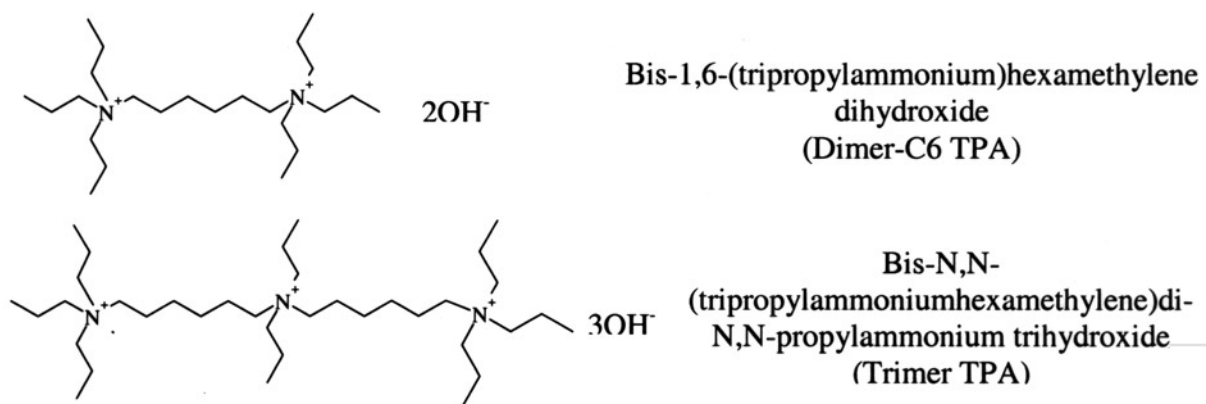


Figure 10. Plot of the fraction of the grain area with the c-axis rotation angle relative to the substrate normal (orientation distribution function).

membrane would be thin and oriented such that straight channels are perpendicular to the substrate. This will allow the molecular sieving to occur along the straight channels, offering the possibility of increased flux. In silicalite-1 crystals, the desirable membrane orientation would be b-oriented. Parametric studies using our simulation models show that in order to obtain a b-oriented membrane, we must identify conditions leading to fast crystal growth along the b-axis. This is equivalent to synthesizing crystals in solution such that their longest dimension is along the b-direction.

Silicalite-1 crystals are typically synthesized in the presence of an organic amine, namely tetrapropylammonium hydroxide (TPAOH), that acts as a structure-directing agent (SDA) or an aid in the formation of its molecular structure. The charge distribution, size, and the geometric shape of the SDA are believed to induce its structure-directing properties¹⁹. The characteristic crystal shape of silicalite-1, using TPAOH as the SDA, is that of a coffin shape (see Figure 5b). Our experimental work on the seeded growth of silicalite-1 crystals, using TPAOH as the SDA, shows that variations in the synthesis conditions (e.g., temperature, silica/organic ratio, silica/water ratio, pH of the solution, etc.) leads to only moderate variations of the coffin shape. The fundamental shape of the crystal remains the same, and the order of the size of crystal dimensions is also constant, with $c > a > b$. Consequently, just changing the membrane synthesis conditions, while still using TPAOH as the structure-directing agent, will likely not result in a membrane with the desired b-orientation.

On the other hand, the work of Beck and Davis²⁰ indicates the potential for a drastic effect on silicalite-1 crystal morphology by using different organic SDAs. These authors performed a systematic study on the influence of tetrapropylammonium (TPA) cations on the synthesis of silicalite-1 nanocrystals. Specifically, they studied the following organic templates:



and found that the different templates affected the crystal morphology at the nanometer length scale. TEM analysis showed that the materials synthesized with the dimer and the trimer are not uniform, single crystals, but aggregates of smaller crystals with non-uniform crystal growth planes. The crystals synthesized in the presence of TPA monomer were nearly spherical particles (~ 75 nm), consistent with our results. In the presence of the dimer, the particles were more sheet-like (~ 50 nm), while synthesis with the trimer yielded clusters of needle-shaped crystals (< 25 nm). While these experiments were conducted for small zeolite nanocrystals that do not develop distinct facets, they provide clear evidence that understanding the roles of different templates provides a unique opportunity for controlling the morphology of zeolite crystals and hence membrane microstructure.

The effect of various templates on the morphology of zeolite crystals is relatively poorly understood. A literature review revealed that during the synthesis of ZSM-23 using pyrrolidine as a template, a contaminant of ZSM-5 of a peculiar shape was reported²¹. This shape, according to the authors, could be best described as an elongated oval with the b-axis longer than the a-axis. The use of dimer-C6 cations in the synthesis of ZSM-5 was introduced in²². The observed crystal shape of silicalite-1 with this template was reported to have a small a/b ratio and a poorly developed morphology²³. NMR experiments show that the SDA was occluded intact within the framework of the zeolite^{20,24}. In addition to the a- crystal direction being poorly developed, the (h0l) and (h00) crystal faces were not expressed.

Molecular mechanics simulations by de Vos Burchart et al. showed that the dimer of TPA preferentially occupies the straight channels of the zeolite²³. These authors proposed that growth occurs by addition of monomers/oligomers of SDA-silica where the dimer TPA cation is attached to the growing framework, sticking only one propyl group inside a straight channel. The next layer is then formed around the N^+-N^+ chain. While the growth mechanism for silicalite-1 is still a subject of debate²⁵⁻²⁷, we believe the faster growth along the b- versus a-axis is still likely caused by the preferred template occlusion within the straight channels of the zeolite.

In order to study the growth of silicalite-1 crystals, we start with a colloidal suspension of calcined seeds that were initially formed in the presence of monomer TPA. The silicalite-1 particles used for the seeding are ~ 100 nm spherical-like seeds that are characterized using SEM. These seeds are then deposited inside a clear growth solution containing water, the template, and a silica source (tetraethylorthosilicate). The seeded growth of initially spherical particles is subsequently monitored over time subject to different growth conditions (i.e., temperature, silica/organic ratio, silica/water ratio, pH of the solution, etc.) and templates. Synthesis temperatures typically range from 90°C - 200°C . The crystal shape and individual

growth rates of the crystal faces are determined using SEM. An average of ~20 crystals are used to calculate the aspect ratio of the growing crystals. XRD experiments give information on the degree of crystallinity of the collected samples.

Preliminary results show that the crystallization rate for the dimer and trimer is slower than that for the monomer. In addition, the crystal morphology using the dimer and trimer is extremely different from the observed shape with the monomer. For both dimer and trimer, the (h0l) and (h00) crystal faces present in the characteristic coffin shape are no longer observed. Instead, we observe fully developed and well-defined elongated oval shaped crystals (see Figure 11). An a/b ratio less than one is observed for a variety of synthesis conditions using both the dimer and trimer of TPA. These results are consistent with the molecular mechanics simulations²³. Moreover, our preliminary results with the trimer shows that under appropriate synthesis conditions the c/b ratio is approaching 1.0 (Figure 11). This offers the possibility of synthesizing, for the first time, silicalite-1 crystals with the b-axis as the longest dimension of the crystal. This can have significant implications for the microstructure and separation characteristics of zeolite membranes grown using these SDAs.

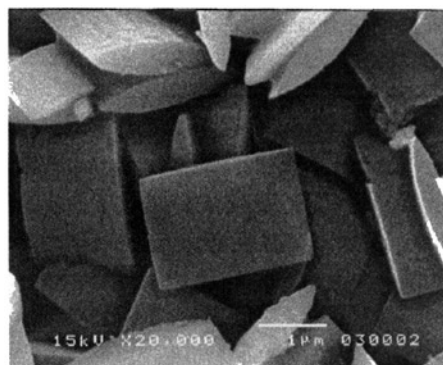


Figure 11. Silicalite-1 crystals grown using the trimer of TPA. Oval shape crystals are observed with b and c-axis approximately equal and short a-axis.

A silicalite-1 membrane was synthesized using the secondary growth technique in the presence of the trimer of TPA. Figure 12 shows the steps in the procedure for the membrane synthesis on an alpha-alumina porous substrate. Figure 12a shows the top view of a typical alumina substrate with a pore size of approximately 200nm. One side of the substrate surface was coated with a smooth mesoporous silica film that has a reduced pore size of about 2 nm by using a sol-gel technique²⁸ (Figure 12b). Then, a b-oriented seed monolayer was deposited on the silica film with the aid of silane coupling agents²⁹ (Figure 12c). From this b-oriented seed layer, a silicalite-1 membrane was obtained by using the secondary growth technique and the trimer of TPA as the template. The x-ray diffraction pattern of the membrane (Figure 13) clearly shows that the preferred orientation in the membrane is now the favored b-orientation that offers the possibility of higher permeation flux.

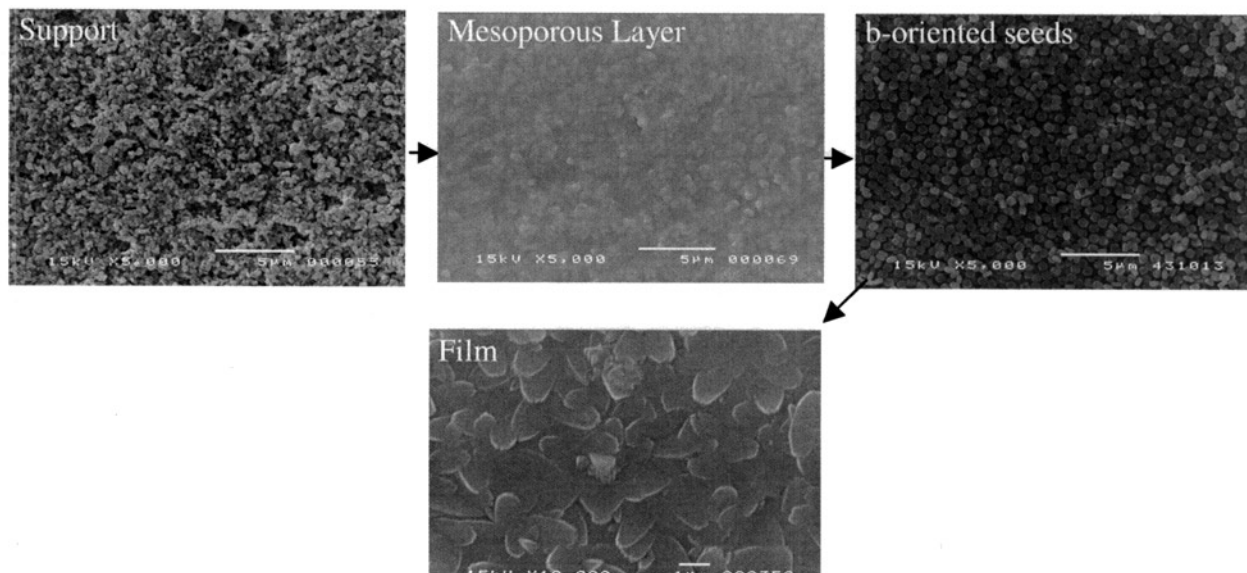


Figure 12. A sequence of SEM images showing the procedure of silicalite-1 membrane synthesis in the presence of the trimer of TPA. The alumina support (a) is coated with a mesoporous layer (b). A b-oriented silicalite-seed layer is deposited (c) and a silicalite-1 film is obtained after hydrothermal synthesis (d).

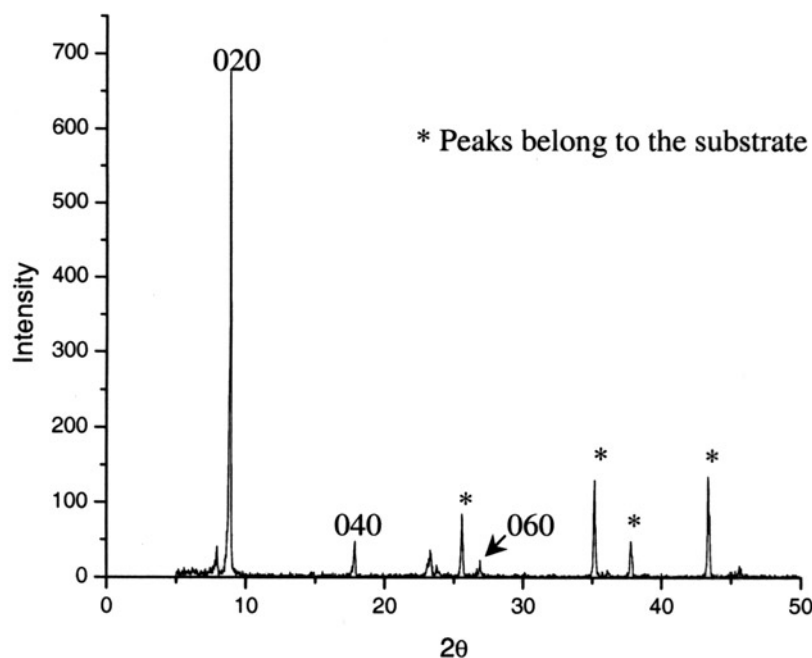


Figure 13. X-ray pattern of the silicalite-1 membrane synthesized using the trimer of TPA as the template. This pattern shows that the silicalite-1 membrane has a b-out-of plane preferred orientation.

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COARSENING IN SOLID-LIQUID MIXTURES 2 : A COMPARISON BETWEEN THEORY AND EXPERIMENT

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Introduction

Ostwald ripening occurs in multi-phase materials and is a diffusional process by which a system lowers its total energy by reducing the total interfacial area. In a two-phase system, large particles grow at the expense of smaller particles. As the system coarsens, the average particle size increases, while the total volume fraction of particles remains constant. Thus, there is a reduction in the average particle density within the system. Ostwald Ripening occurs in many two-phase mixtures, including precipitate hardened alloys, and can significantly affect the materials properties. For example, as coarsening progresses, the decreased particle density leads to a degradation of the mechanical strength of precipitation hardened alloys.

Until recently there was little agreement between coarsening experiments and coarsening theory. The main difficulty in comparing theory to experiment is selecting a materials system that meets the criteria of the theory: mass transport that is diffusion controlled, low volume fraction of particles, an isotropic interfacial energy (spherical particles) and a stress-free matrix. In addition, for a practical experiment, the diffusion rate should be sufficient so that a large change in particle radius can be measured in a reasonable amount of time. Meeting all these requirements, especially the interfacial energy and stress free matrix requirements, in two-phase solid mixture becomes very difficult. Thus, we look to solid-liquid systems.

The solid-liquid system that has been identified as an ideal system to test theory is a mixtures of Sn particles in a Pb-Sn eutectic matrix. This system meets all of the necessary requirements, and a large change in particle radius can be achieved over a relatively short time. In addition, all the physical parameters needed for comparison to theory are known. However, the density difference between the solid and liquid leads to a high degree of particle sedimentation. Hardy and Voorhees investigated the coarsening of tin particles in a Pb-Sn matrix in high volume fraction mixtures [1]. These experiments were performed with a high volume fraction of coarsening phase, which limits particle sedimentation, but also leads to a high number of particle contacts in the system, for which the theories do not account.

Coarsening in Solid-Liquid Mixtures Experiment

In 1997 the Coarsening in Solid Liquid Mixtures (CSLM) experiment was performed aboard the Space Shuttle Columbia (STS-83 and STS-94). Due to the microgravity environment, the sedimentation of Sn particles was avoided (Figure 1).

Keywords: coarsening, Ostwald ripening, solid-liquid mixtures, flight

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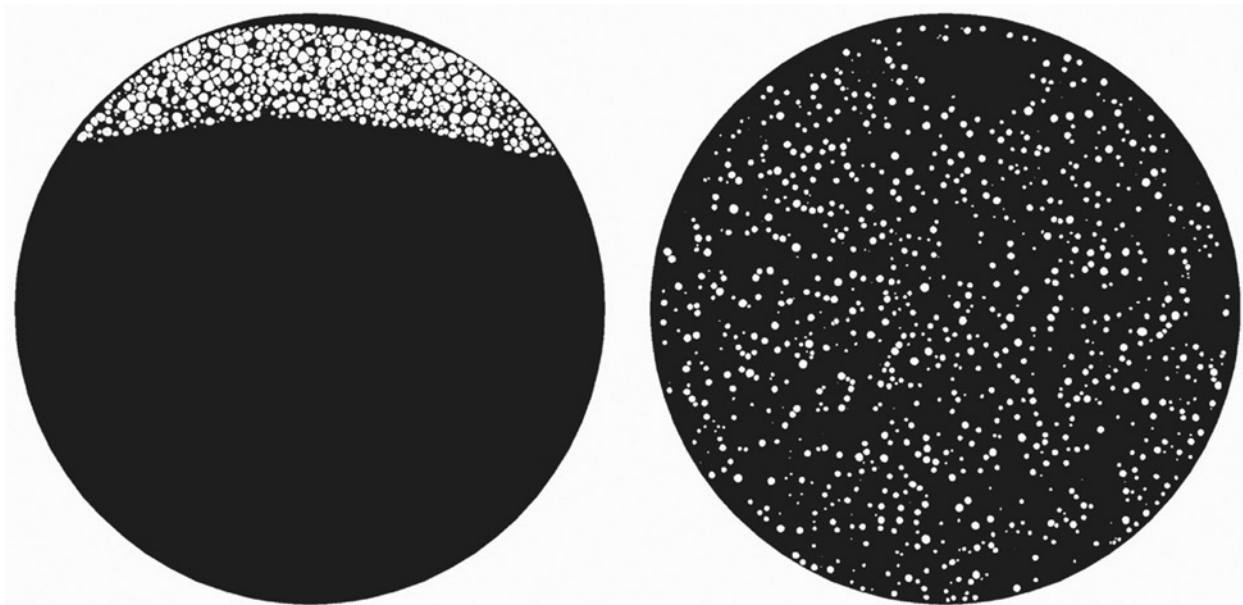


Figure 1. On the left we the microstructure of a ground-processed solid-liquid mixture after 10 hours of coarsening. Right, the microstructure of a 10% solid phase sample coarsened for 10 hours in a microgravity environment. The particles are white; the matrix is black. The entire cross-section of 1cm diameter sample is shown.

In the experiment, we study the coarsening on Sn-rich particles in a Pb-Sn liquid, over a range of volume fractions from 0.1 to 0.8. The low volume fraction experiments will allow for direct comparison to theory. The higher volume fractions will allow us to examine the effect of the skeletal structure on the coarsening process.

Results

We will briefly review the results here (for complete results see [2-4]). Below we have plotted the normalized Particle Size Distribution (PSD) for several volume fractions, ϕ , over several different coarsening times. In volume fractions lower than $\phi = 0.3$, we compared the results to the steady state Akaiwa-Voorhees (AV) theory [5]. Above $\phi=0.3$ the system must have a significant number of particle-particle contacts, thus the AV theory does not make predictions above $\phi = 0.3$. Therefore, we compared the higher volume fractions to the Marsh and Glicksman (MG) theory [6], which does make predictions above 30 volume percent. We can see that at all volume fractions there are significant discrepancies between the experimental results and the theories, and that this discrepancy increases with volume fraction. Also, steady-state coarsening theory tells us that the normalized PSDs should not evolve over time. However, at $\phi = 0.1$ we see that that the tail and peak of the PSD evolves with time and appears to be approaching the steady-state solution. In the $\phi = 0.3$ plot, we see that the evolution of the PSD towards steady state is much slower. In the $\phi = 0.8$ plot there is no observable evolution of the PSD over time.

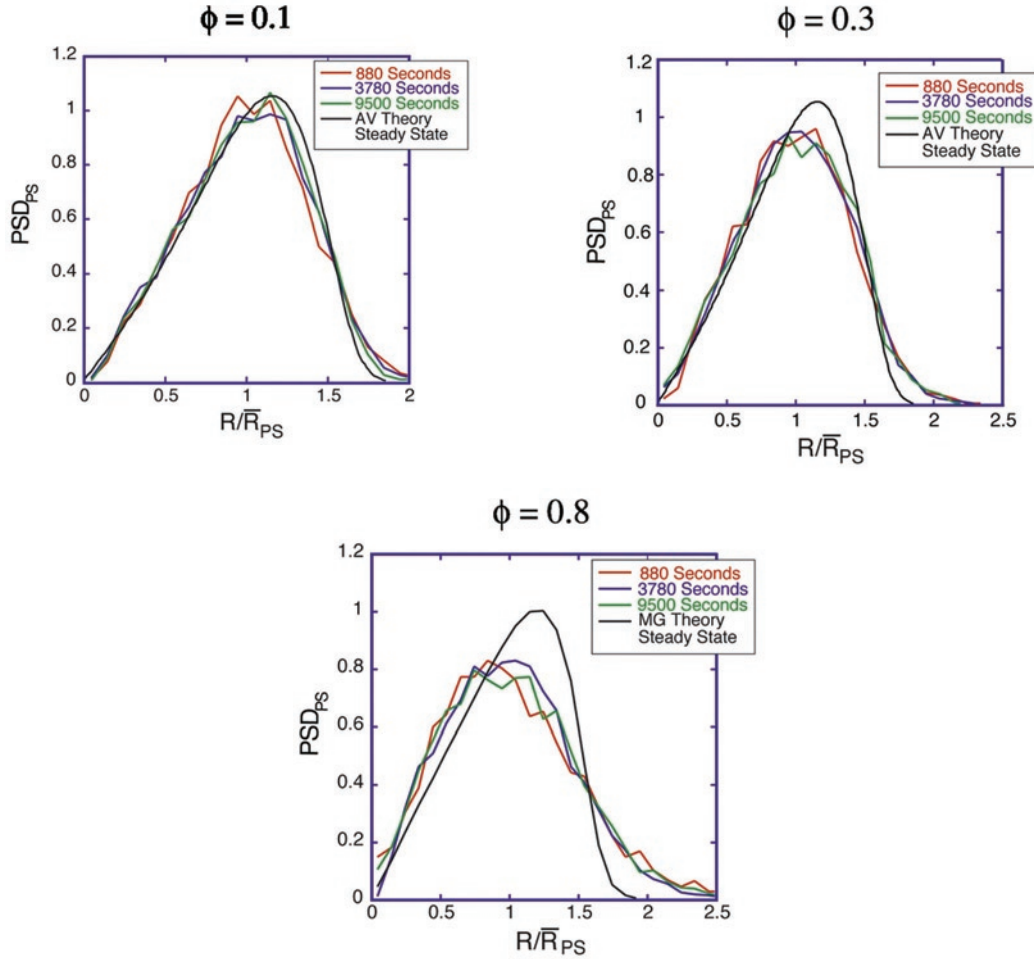


Figure 2. Here we see the scaled Particle Size Distribution (PSD) for several different volume fractions, ϕ , plotted against the plane section particle radius over the average plane section particle radius ($R/\bar{R}_{pS}$). We have compared the experimental results to coarsening theory. In the lower volume fractions we compare to the Akaiwa-Voorhees theory (AV). We compare the higher volume fractions to the Marsh and Glicksman theory (MG).

Thus, we have the trend of the overall temporal evolution rate of the PSDs with volume fraction; at lower volume fractions the PSDs evolves toward the steady-state conditions faster than at higher volume fractions.

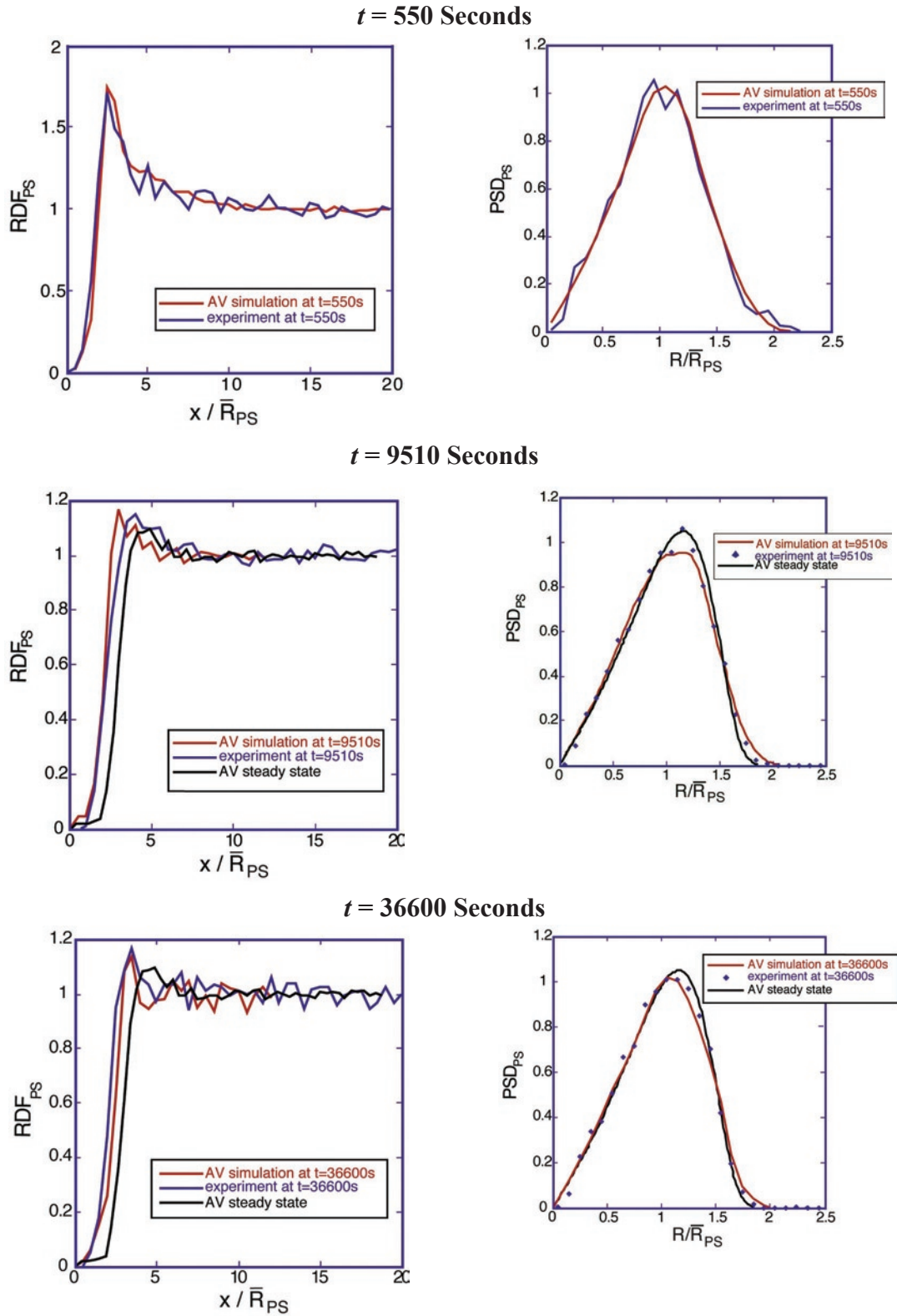


Figure 3. Normalized RDF and normalized PSD for $\phi=0.1$. The experimental results are compared to Akaiwa-Voorhees steady-state simulation and a transient simulation that accounts for the spatial distribution of the particles.

We also measured the normalized Radial Distribution Function of the system. The RDF measures the spatial distribution of the particles, which indicates the amount of clustering in the system. Steady-state theories predict that the normalized RDF will not evolve over time, and any initial transient regime is relatively short. We compare the experimental results to two theories, the steady-state AV theory, and the transient AV simulation that accounts for the evolution of the spatial distribution of the particles during coarsening.

The PSDs and scaled Radial Distribution Function (RDF) for $\phi = 0.1$ at several coarsening times is plotted in Figure 3. The evolution of the microstructure is shown even more clearly in the change of the normalized RDFs. Initially there is a large peak, near $x / \bar{R}_{ps} = 2$, which indicates that initially the particles were clustered. We see that as time progresses, the peak decreases, while the exclusion zone, the region around the particles that is nearly particle free, increases and begins to approach the steady state value. This indicates that the particles are becoming more isolated as the coarsening process continues.

Not only does the AV simulation more closely match the experimental RDFs, but it also reproduces the evolution of the PSD towards the steady state solution. This shows that the transients are very long, and that the system is undergoing transient coarsening.

Coarsening in Solid Liquid Mixtures 2

CSLM2 seeks to further explore the transient regime using longer coarsening times. To accommodate the longer experiment times, the experiments will be performed on the International Space Station (ISS).

The limiting factors for the experiment are now the microgravity environment aboard the ISS, which will allow the samples to be coarsened up to 48 hours. Our shortest coarsening time will overlap with CSLM, so that we can directly compare between the two experiments. We expect to reach a factor of ten increase in the average particle size at lower volume fractions, and even greater at the high volume fraction samples. We also want to investigate the rate of evolution of the scaled PSDs and RDFs, especially at higher volume fractions.

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MODELS TO OPTIMIZE THE BENEFITS OF STEADY AND ROTATING MAGNETIC FIELDS FOR CRYSTAL GROWTH IN MICROGRAVITY

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1. Introduction

Both steady and rotating magnetic fields have been proposed for crystal-growth furnaces currently being designed for future experiments on the International Space Station (ISS). A steady magnetic field with a strength of 0.1-0.2 T would be produced by a solenoid placed around the crystal-growth furnace. A steady magnetic field can stabilize and tailor the thermocapillary and solutocapillary convections in the floating-zone and detached Bridgman processes. It can also damp the buoyant convection driven by g-jitters and steady residual accelerations. A rotating magnetic field (RMF) would be produced by inductors which are placed with equal azimuthal spacing around the furnace and which are connected to the successive phases of a multiphase AC power source. An RMF is an essentially spatially uniform transverse magnetic field which has a strength of 1-10 mT and which rotates around the furnace's centerline at 50-400 Hz. The azimuthal melt motion produced by an RMF can stabilize thermocapillary and buoyant convections through the Taylor effect, and it can drive a controllable radial velocity near the crystal-melt interface, thus producing radial uniformity of dopants and species in crystals. During the last two years, we have developed models to optimize the benefits of steady and rotating magnetic fields for future crystal-growth experiments on the ISS.

2. Steady Magnetic Field Stabilization

There have been several previous attempts to treat the stability of buoyant or thermocapillary convection in a cylindrical geometry with a steady, uniform, axial magnetic field. Unfortunately these previous models were only accurate for very weak magnetic fields, e.g., $Ha < 15$, where Ha is the Hartmann number which is proportional to the magnetic field strength. For proposed crystal-growth processes with steady magnetic fields, $Ha = 100-1000$. We have developed methods to obtain accurate results for all field strengths. Our first key step involves the centerline at $r = 0$ in the cylindrical geometry. We discovered that accuracy is greatly improved when (1) the spectral representation of each variable has the correct Taylor series expansion in r , and (2) each governing equation is divided by the appropriate power of r and is applied at $r = 0$. For a typical critical flow, this step reduces the relative truncation error from $1.E-5$ to $1.E-10$, and increases the maximum value of Ha for accurate results from the fully numerical approach with reasonable computational resources from 15 to 100. Our second key step is the development of a hybrid approach which combines an analytical solution for the Hartmann layers adjacent to liquid-solid interfaces which are not parallel to the magnetic field, and a numerical solution for the rest of the liquid domain. Since Hartmann layers become very thin as the Hartmann number is increased, there is an exponential increase in the number of grid points needed for accurate results from a fully numerical approach. Our hybrid approach yields accurate results for large values of Ha with moderate computational resources.

Keywords: modeling, magnetic fields, instability, theoretical

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Our first application of these two new steps involved the Rayleigh-Benard instability in a vertical cylinder with a vertical magnetic field [1]. With our first step, we obtained accurate results from the fully numerical approach for $Ha < 100$. With our hybrid approach, we obtained accurate results for $50 < Ha < 500$. Our asymptotic solution for $Ha \gg 1$ gave accurate results for $Ha > 300$. The agreement between these three different approaches in their overlap regions validated the accuracy of each approach. We have successfully applied our first step to the magnetic stabilization of the buoyant convection in a crystal-growth process [2] and to the magnetic stabilization of the thermocapillary convection in the floating-zone process [3]. We are currently developing hybrid and asymptotic approaches for both of these problems.

We found that no one had previously treated the stability of the solutocapillary convection in the floating-zone process with or without a magnetic field. The solutocapillary instability is fundamentally different from the thermocapillary instability (1) because the boundary conditions on the solute concentration at the liquid-solid interfaces are quite different from those for the temperature and (2) because the solute transport due to the melt flow from the feed rod to the crystal is not negligible. We began with an accurate treatment of the instability of the solutocapillary convection in the floating-zone process without a magnetic field [4].

3. Floating-zone GeSi With Strong Steady Magnetic Field

Recent experiments have shown that the solutocapillary convection sometimes overwhelms the thermocapillary convection during the floating-zone growth of alloyed crystals with 5-10% silicon and 90-95% germanium (GeSi). We developed a model for the floating-zone growth of GeSi crystals with a strong, steady, uniform, axial magnetic field [5]. This model showed (1) that two different stable steady melt motions are possible for the same growth conditions and (2) that the flow which occurs in an actual process depends on the history of the process. If the thermocapillary convection is established before the solutocapillary convection is added by rejection of germanium into the melt during crystallization, then the strong mass transport prevents the development of a significant concentration gradient along the free surface, so that the thermocapillary convection remains dominant. On the other hand, if the thermocapillary convection is temporarily suppressed by increasing the magnetic field strength, then a free-surface concentration gradient develops which continues after the magnetic field strength is reduced to its original value, so that the solutocapillary convection is dominant.

4. Species Transport During Bridgman Growth Of GeSi With A Steady Magnetic Field

A major problem for the Bridgman growth of alloyed crystals, such as GeSi, is the nonuniformity of the two species in the crystal. A steady, uniform, axial magnetic field may dramatically reduce both radial and axial macrosegregation. With even a moderate magnetic field strength, transient effects in the temperature and melt motion are negligible, so that both are accurately modeled with quasi-steady-state solutions for each moment during the process [6]. However, species transport is an intrinsically transient process and must be accurately modeled for the entire period of time required to grow a crystal. Our important contribution is to use quasi-steady-state solutions for the temperature distribution and melt motion in a transient model for the species transport for the Bridgman process with a steady axial magnetic field [7,8].

5. Thermoelectromagnetic Convection

During any crystal-growth process, radial macrosegregation of a dopant or of one species can lead to a significant temperature variation along the crystal-melt interface. For most semiconductors at their melting temperature, the absolute thermoelectric power S for the solid is much larger than that for the liquid. The

combination of a difference in the values of S for the liquid and solid and a temperature gradient along the crystal-melt interface leads to a circulation of thermoelectric current through the crystal and melt. If a steady magnetic field is applied to stabilize and control the thermocapillary or buoyant convection, then this field interacts with the thermoelectric current to drive an additional melt motion, which is called the thermoelectromagnetic convection (TEMC). In a study of steady, axisymmetric TEMC [9], we showed that there are two distinctly different types of TEMC, depending on the strength of the magnetic field. For a sufficiently weak magnetic field, the melt motion has no effect on the thermoelectric current. Therefore the model involves two sequential problems: first the solution for the thermoelectric current distribution and second the solution for the melt motion with a known azimuthal body force due to the magnetic field and thermoelectric current. On the other hand, for a moderate magnetic field strength, the melt motion affects the thermoelectric current, and this magnetohydrodynamic flow involves an intrinsic coupling of the flow and electric current.

One characteristic of the solutions assuming an axisymmetric crystal-melt interface temperature variation is that the azimuthal velocity is much larger than the radial and axial velocities. This suggests that a slight deviation from axisymmetry in the interface temperature might lead to a very different melt motion. Since the interface temperature variation arises from the lateral macrosegregation of a dopant or species and since this lateral macrosegregation is generally not axisymmetric, the assumption of an axisymmetric interface temperature, which has been included in all previous treatments of TEMC, appears unrealistic. In our most recent study of TEMC [10], we showed that a nonaxisymmetric crystal-melt interface temperature variation with a strong, uniform, axial magnetic field does indeed lead to a melt motion which is very different from that for an axisymmetric interface temperature.

6. Effects Of RMF On Gas Transport In The Detached Bridgman Process

For both experimental crystal growth in space and commercial crystal growth on earth, various processes have both advantages and disadvantages, so that no one process is clearly superior to all the others. The major disadvantages are: (1) for the floating-zone process, the thermocapillary instability leads to striations in the crystal, (2) for the liquid-encapsulated Czochralski process, there is radial macrosegregation of dopants, as well as striations due to the buoyant instability, and (3) for the Bridgman process, there are many crystal defects, such as dislocations and twins (in InP), due to the contact between the crystal and the ampoule wall. In the detached Bridgman process, the melt has a short free surface between the ampoule wall and the periphery of the crystal-melt interface, so that the crystal diameter is slightly smaller than the ampoule diameter. Due to the melt's local detachment from the ampoule, there is no contact between the crystal and ampoule, so that there are far fewer defects in the crystal. In addition, the free surface is so short that the thermocapillary and solutocapillary convections are stable, so that their instabilities do not lead to striations in the crystal. If the detached Bridgman process can be developed for commercial crystal growth, it will have a clear advantage over other processes for both important compound semiconductors, such as indium-phosphide (InP), and for alloyed semiconductors, such as SiGe. Unfortunately the mechanisms responsible for detachment are not well understood. One theory is that gases dissolved in the melt are rejected during solidification and then evaporate at the periphery of the crystal-melt interface to produce the gas pocket supporting the detached free surface.

We developed a model for the effects of an RMF on the gas transport during the Bridgman process in microgravity [11]. The results showed that an RMF decreases transport of gases rejected at the crystal-melt interface to the detached free surface, and thus an RMF should be detrimental to detachment in

microgravity. The only experiments involving detachment with an RMF have been done on earth and are clearly dominated by buoyant convection which was not included in our model for microgravity [11]. In these terrestrial experiments, an RMF has sometimes led to detachment and sometimes terminated detachment. Further modeling and more experiments are needed before detachment can be understood and achieved in commercial processes. Good agreement between model predictions and the results in terrestrial experiments should validate the models for the design of experiments for the ISS.

7. High Frequency RMF

For an RMF, low frequency means that the magnetic field produced by the electric currents in the melt is negligible so that magnetic field due to the external inductors penetrates throughout the melt. Most previous models of RMF's have assumed a low frequency, but it was not apriori obvious that a higher frequency would not lead to a melt motion which might be more beneficial for the crystal. First we developed a very accurate hybrid method to compute the magnetic field distribution when the field produced by the electric currents in the melt is partially cancelling the field produced by the external inductors [12]. Second we computed the melt motion driven by a high-frequency RMF and treated the stability of this flow [13]. The results showed that higher frequencies lead to less desirable melt motions and to a more unstable flow. Clearly the model indicates that an expensive experiment to investigate high-frequency RMF's in crystal growth would be a waste of time and money. For the planned crystal-growth experiments on the ISS, 400 Hz is a low frequency because the diameter of the melt in each experiment will be small.

8. Combining an RMF with Crystal Rotation

One advantage of an RMF over a steady magnetic field is that an RMF produces a controllable melt circulation while a steady magnetic field can only damp the buoyant and thermocapillary convections. One objective is to tailor the RMF-driven flow in order to achieve a uniform radial distribution of dopants and species in crystals. Most previous studies of mass transport with RMF's have assumed that the crystal-growth system does not rotate, so that the axial variation of the azimuthal velocity driven by the RMF produces a radially inward flow near the crystal-melt interface. For many processes, a radially outward local flow is needed to achieve a radially uniform crystal composition. One option is to apply a steady, weak, transverse magnetic field and to rotate the crystal-growth system about its centerline. The steady magnetic field reduces the azimuthal velocity driven by the crystal rotation, so that axial variation of the azimuthal velocity drives a radially outward flow near the crystal-melt interface [14]. Unfortunately this approach leads to a nonaxisymmetric melt motion which produces two striations in the crystal with each rotation [15]. The optimal solution is to rotate the crystal in one azimuthal direction and to apply an RMF in the opposite azimuthal direction [16]. The RMF reduces the azimuthal velocity produced by the crystal rotation and thus achieves the desired controllable radially outward flow near the crystal-melt interface. Since the RMF rotates at 50 Hz or more, the melt does not respond to its high-frequency, nonaxisymmetric body force, so that the melt motion remains axisymmetric until the RMF instability occurs.

9. RMF Control of Thermocapillary Convection

The current interest in RMF's arose from the floating-zone growth of silicon crystals with a variable-strength, 50 Hz RMF. As the strength of the RMF was increased, the striations changed dramatically: the difference between the maximum and minimum dopant concentrations decreased and the spacing between adjacent maxima decreased, reflecting an increase in the frequency of the periodic melt motion. Therefore the RMF did not eliminate the thermocapillary instability, but it altered the periodic melt motion arising from this instability so that its deleterious effects on the crystal were greatly decreased. The mechanisms

for this improvement are not currently understood, and a great deal of future experimental and modelling studies will be needed to reproduce and optimize the benefits of an RMF in the floating-zone process. The meridional circulation (with the radial and axial velocities) driven by the thermocapillary convection or by an RMF separately are in the same directions. Therefore some researchers conjectured that the magnitude of the meridional circulation with both thermocapillary convection and an RMF would increase monotonically as the strength of the RMF is increased from zero. However, we developed a model which showed that as the strength of the RMF is increased from zero, the magnitude of the meridional circulation first decreases dramatically due to the Taylor effect associated with the azimuthal velocity produced by the RMF [17]. The meridional circulation reaches a minimum at some RMF strength and then approaches the flow for the RMF alone. This indicates that for each process, there is an optimal RMF strength with the most stabilizing effect and with the greatest improvement in crystal quality. Clearly much more research is needed.

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PROCESS-PROPERTY-STRUCTURE RELATIONSHIPS IN COMPLEX OXIDE MELTS

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This project is a fairly broad-based investigation of the behavior of molten oxide materials under highly non-equilibrium conditions accessed using containerless techniques. The work is exploring new directions in materials processing which show promise for development of low gravity experiments requiring pristine liquid surfaces and quiescent liquids to decouple convective and diffusive transport. Emphasis is being placed on investigation of alumina-based materials and the research includes: (i) substituting nitrogen for part of the oxygen in the liquids, (ii) determining glass forming behavior, and (iii) measurement of the structure of the glasses and liquids. Experiments are being performed at CRI and in collaboration with scientists at NASA and NASDA to establish requirements for glass formation and evaluate requirements for measurements of liquid properties, in particular the melt viscosity, using levitation techniques. Collaborations with scientists at Argonne National Laboratory, University of California-Davis and the Food and Drug Administration are providing important information about the structure and properties of the new materials which are resulting from this research.

Major activities were:

1. Construction and testing of a high pressure aerodynamic levitator for investigation of oxynitride liquids at pressures up to 5 bar.
2. Synthesis of novel oxide and oxynitride glasses.
3. Establishing conditions for electrostatic levitation of oxide liquids.
4. Investigation of the structure of oxide liquids using neutron diffraction in collaboration with scientists at Argonne National Laboratory.

The experimental activities and results of the research are summarized in the following sections of the report. Scientific papers on the work have been submitted or are being prepared. Results of the work were presented at international conferences on materials and microgravity experimentation. The basic research performed in this work is leading to investigation of new high dielectric constant materials and novel optical and photonic glasses. Crystallization of the glassy materials offers a means to produce very fine scale crystalline microstructures.

1. Construction and Testing of a High Pressure Aerodynamic Levitator

An aerodynamic levitator which can operate at pressures of up to 5 bar (~75 psi) in a controlled atmosphere (see Figure 1) was developed and constructed at CRI. Samples were levitated in a metered stream of process gas and heated from above with a partially-focused continuous wave CO₂ laser beam. Sample temperature, video images of the levitated samples, the levitation gas flow rate and total pressure in the system were acquired by computer.

Keywords: oxides, oxynitrides, liquids, containerless, structure.

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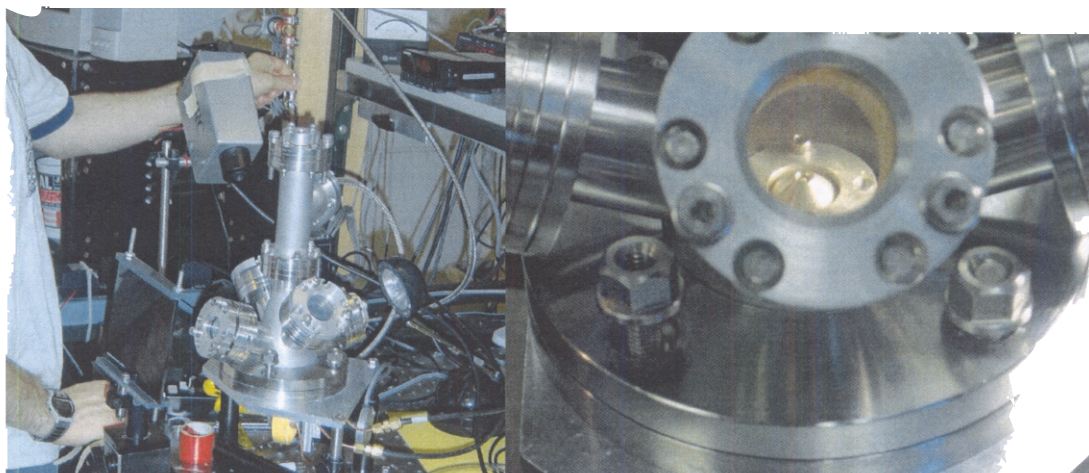


Figure 1. Left: overall view of the “HP” aerodynamic levitator. The system uses a 250 Watt cw CO₂ laser for heating the levitated sample. The sample temperature is monitored with an automatic optical pyrometer operating at a wavelength of 900 nm (seen to the left of the stainless steel chamber). Right: close up view of levitation chamber with the levitation nozzle visible through an optical window.

2. Synthesis of Novel Oxide and Oxynitride Glasses

Calcium aluminate eutectic (CAE, Ca₁₆Al₁₈O₄₃), melting point 1625 K¹, was used as a test material for development of ESL and structural measurement experiments. Compositions of selected oxynitride materials which were studied in the pressurized aerodynamic levitator are given in Table I.

Table I. Composition of oxynitride materials, values are given in mole %.

Empirical formula	Al ₂ O ₃	AlN	Y ₂ O ₃	SiO ₂	Mole % N
Y ₁₂ Al ₂₀ O ₄₅ N ₂	52.9	11.8	35.3	-0-	4.4
Y ₆ Al ₁₀ O ₂₁ N ₂	44.4	22.3	33.3	-0-	9.5
Y ₂₄ Al ₄₀ O ₈₁ N ₁₀	40.5	27.0	32.5	-0-	12.3
Y ₃ Al ₅ O ₉ N ₂	30.0	40.0	30.0	-0-	22.2
Y ₃ Al ₁₀ Si ₃ O ₂₄ N	35.0	10.0	15.0	30.0	4.2
Y ₆ Al ₁₉ Si ₆ O ₄₅ N ₃	40.0	15.0	15.0	30.0	6.7
Y ₁₀ La ₁₀ Al ₅₀ Si ₁₅ O ₁₁₇ N ₁₂	56.8	-0-	11.4	13.6*	10.2

*11.4 La₂O₃, 6.8 Si₃N₄.

Samples were made by mixing high purity powders and pressing the mixtures into pellets 2-3 mm in diameter suitable for the levitation experiments. Use of “AlON”² (Al₂₃O₂₇N₅), provided by Dr. Parimal Patel at Army Research Laboratory, as a source of nitrogen is under investigation.

Conditions were established for levitation of molten samples at pressures from 1-5 bar in UHP nitrogen. The gas flow rate required for stable levitation increased with increasing pressure. At lower pressures ~1 bar, outgassing of the nitrogen-bearing compositions occurred and it was accompanied by bubbling as the sample was melted. At higher pressures, outgassing was suppressed and yellow, brown and black glasses were formed. Nitrogen analyses and experiments on pure AlON samples are in progress.

3. Establishing Conditions for Electrostatic Levitation of Oxide Liquids.

The extension of ESL techniques to work on molten oxides at very high temperatures is needed to study the viscosity, surface tension, density and other properties of the liquids which are of interest in connection with development of new materials and interpretation of liquid structure measurements. An ESL is a candidate instrument for the International Space Station and establishing ground-based capabilities for experiments on liquid oxides will support development of new flight experiments. In this work, experiments were performed at NASDA Tsukuba Space Center to investigate the application of a pressurized ESL instrument³ to levitation of molten CAE material⁴. Prior experiments in the high vacuum ESL facility at NASA Marshall Space Flight Center showed that levitation was limited to temperatures below the melting of the oxide material, possibly due to evolution of dissolved gases which resulted in variations in the charge on the sample⁵.

Spheroidal samples of CAE 1.5-2 mm in diameter were placed on an aerodynamic diffuser located in the lower ESL electrode. The ESL process chamber was pressurized to 4 bar with UHP-grade nitrogen. Levitation was initiated by a flow of $\sim 200 \text{ cm}^3/\text{min}$. of nitrogen through the diffuser. The sample was slowly heated with a CO_2 laser beam and its temperature was measured with an automatic optical pyrometer. Thermionic emission resulted in loss of electrons and the sample became positively charged after a few seconds. ES levitation was initiated when a voltage of 8-10 kV was applied between the levitator electrodes. The levitated sample was melted by increasing the incident heating power.

Samples of the CAE material were levitated using potential gradients of 8-10 kV/cm between the levitator electrodes. Even at the highest voltages gradients investigated, $\sim 15 \text{ kV/cm}$, and with the sample at up to 1850 K, there was no evidence of charge loss from the levitated sample. Stable levitation was maintained for periods of up to about 1 hour before termination by reducing the voltage gradient. During levitation of the liquid, no rotation or oscillation of the sample was observed in the video images. The high degree of sample stability in the levitated samples was attributed to damping and viscous drag by the pressurized gas. Figure 2 shows a CAE sample levitated in the pressurized ESL system⁴.



Figure 2. Images of a levitated CAE-composition sample in the high pressure ESL at a pressure of 4 bar of UHP nitrogen (see also ref. 3 and 4). The sequence (left to right) shows a molten sample backlit with an incandescent light, a molten sample illuminated by self emission, and a backlit glass sample made *in-situ*. The sample was remelted several times while maintaining stable levitation.

The condition for electrostatic levitation is:

$$mg = Q \frac{dE}{dz}$$

Where m is the sample mass, g is the gravity vector, Q is the charge on the sample, and dE/dz is the electric field gradient along the gravity vector. For typical CAE samples, the field gradient was 8-10 kV/cm, thus Q was $\sim 10^{-9}$ C.

The use of the aerodynamic diffuser meant that the sample charged by thermionic emission of electrons rather than as a result of contact with the lower ESL electrode. For a typical CAE sample with a surface area of ~ 0.1 cm², levitation occurred after 30 s at 1100 K. To achieve a charge of $\sim 10^{-9}$ C, the effective charge transfer rate during the transient charging step was $\sim 3.3 \times 10^{-11}$ C/cm²•s. The work function of the sample at 1100 K can thus be estimated from the relationship:

$$J = AT^2 e^{-\frac{\Phi}{kT}}$$

where J is the charge transfer rate in C/cm²•s, A is a constant = 120 A/cm²K², T is the absolute temperature, Φ is the work function, and k is Boltzmann's constant. The derived value of the work function of the CAE material at 1100 K is 3.7 eV.

4. Investigation of Liquid Structure Using Neutron Diffraction*

We are interested in the structure of non-equilibrium materials, both glasses and liquids, formed from the aluminate compositions. Neutron diffraction is well suited to the study of oxides and oxynitrides nitrides because of the large coherent scattering lengths of oxygen and nitrogen. X-ray techniques provide complementary data due to the relatively larger scattering contribution by heavier elements. Preliminary test experiments were performed to investigate the feasibility of determining the structure of levitated liquids using pulsed neutron diffraction. Work was performed in collaboration with Dr. Chris Benmore at the Glass Liquids and Amorphous materials Diffractometer (GLAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory⁶. Samples of CAE liquid were levitated at a temperature of 2000 K for a total period of 20 hours to obtain sufficient neutron data to determine the structure factor of the liquids⁷.

*work partially supported by DOE under contract numbers: DE-FG02-01ER86121 and W-31-109-ENG-38.

Planned Activities

Plans for the ongoing research are outlined below.

Optimize and implement procedures for the synthesis of nitrogen-doped glasses.

Study the properties of the liquids. It is expected that substitution of nitrogen for part of the oxygen in the materials will develop a covalent character and lead to directional bonding with a corresponding change in melt viscosity. Measurements of liquid viscosity, especially in the non-equilibrium liquids, is a high priority. Viscosity measurements obtained from fiber pulling experiments are subject to effects of high shear rates which occur in the liquids during the fiber pulling operations. ESL experiments to investigate liquid drop oscillation methods for measurement of viscosity are being planned.

Investigate the structure of glasses as a function of composition and synthesis conditions. We are applying several techniques to study the structure of samples including X-ray and neutron diffraction, NMR and Raman spectroscopy.

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MICROGRAVITY STUDIES OF LIQUID-LIQUID PHASE TRANSITION IN UNDERCOOLED ALUMINA-YTTRIA MELTS

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This research concerns the behavior of molten pseudo-binary alumina-yttria (A-Y, Al_2O_3 - Y_2O_3) materials under non-equilibrium conditions. These oxides form liquids with a highly non-Arrhenian temperature-viscosity relationship¹, some compositions undergo a polyamorphic liquid phase transition to form two immiscible liquids^{2,3}. When the liquid mixtures are quenched, two-phase glasses are formed in which both phases have virtually identical chemical compositions. The A-Y based glasses are of interest for laser and optical applications and they are of fundamental and applied interest in materials science. The overall goal of this investigation is to increase understanding of phase behavior in oxide liquids, better understand the nature of liquid phase transitions, and investigate the way in which the melt viscosity changes with temperature. Low gravity experiments are of interest because they can access “pristine” and quiescent liquid samples needed to investigate subtle changes in liquid properties. The ground-based flight definition research is being performed in facilities that access the highly non-equilibrium liquid by using containerless techniques. This research has led to development of new high-dopant content optical glass materials which are being commercialized in separate work. Liquids and glasses are being characterized as a function of the process conditions and the viscosity of the liquids is being investigated using stinger and drop oscillation techniques at CRI and in collaboration with scientists at NASA and NASDA. The structure and properties of the glasses are being studied in collaborative investigations using scanning electron microscopy, X-ray and neutron diffraction, ²⁷Al NMR, thermal analysis, and optical spectroscopy. A model of the liquid structure is being developed. Main findings of the work are summarized below:

1. The undercooling limit for the liquid of the YAG-composition (under containerless conditions) is *ca.* 0.58 times the melting point of the crystal.
2. The phase transition occurs *via* changes in the connectivity of the Al-O and Y-O coordination polyhedra and changes in Y-O coordination which preserve stoichiometry.
3. Processing and composition changes which promote formation of predominantly 4-coordinate Al^{3+} ions tend to stabilize single phase glasses.
4. Based on limited viscosity data, the fragility index of the liquids is 0.43-0.65. The glass transition temperatures are practically constant over the range of A-Y materials studied.

Activities were focused on detailed characterization of the structure and properties of single- and two-phase glasses to establish the experimental requirements for development of a fuller understanding of the liquid-liquid phase transition in the ionic alumina-yttria liquids. The research is developing a precise analysis of the requirements for low gravity experiments on A-Y liquids needed to study the phase transition kinetics.

Keywords: glass, phase transitions, viscosity, containerless, flight.

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The work included collaborative research with scientists at NASA Marshall Space Flight Center and NASDA Tsukuba Space Center, SUNY Stony Brook, Argonne National Laboratory, University of Missouri-Rolla and University of California at Davis.

The major accomplishments were to:

1. Establish the composition range for formation of single- and two-phase glasses in the $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ system using containerless processing techniques³.
2. Investigate the structure of single- and two-phase glasses using high energy X-ray diffraction pulsed neutron diffraction⁴.
3. Model the structure of the glasses using reverse Monte-Carlo simulations constrained by the measured X-ray and neutron structure factors.
4. Investigate the structure of single- and two-phase glasses using ^{27}Al NMR^{5,6}.
5. Perform thermal analysis of the glasses to establish glass transition, phase transition and crystallization temperatures⁷.
6. Perform Electrostatic Levitation (ESL) experiments to: (i) determine conditions for levitation of liquid $\text{Y}_3\text{Al}_5\text{O}_{12}$, (ii) measure the density of the melt as a function of temperature, and (iii) establish the feasibility of measuring surface tension and viscosity of the liquid by drop oscillation techniques.

Scientific papers on the work have been submitted or are being prepared. Results of the work were presented at international conferences on materials and microgravity experimentation. The basic research performed in this work has resulted in a patent on single phase rare earth aluminate glasses. Commercial applications of the REAl™ glasses in communications, medical laser and military applications are being developed in separately supported research and development. The following sections give details of the experiments and results.

1. Glass forming composition range

Glass formation was investigated using aerodynamic and aero-acoustic levitation in combination with continuous-wave CO_2 laser beam heating of the samples. The glass forming range for samples processed under containerless conditions was 58-77 mole % alumina. Two-phase glasses were formed from most of the compositions with a narrow range, from approximately 71-73 mole % alumina, where single-phase glasses are formed. At the limits of the glass forming range, the critical cooling (R_c) required to prevent crystallization was approximately 300 K/s. Samples which were cooled at rates less than R_c spontaneously crystallized. Figure 1 presents the alumina-rich portion of the pseudo-binary alumina-yttria phase diagram. The glass forming range under investigation is marked on the diagram.

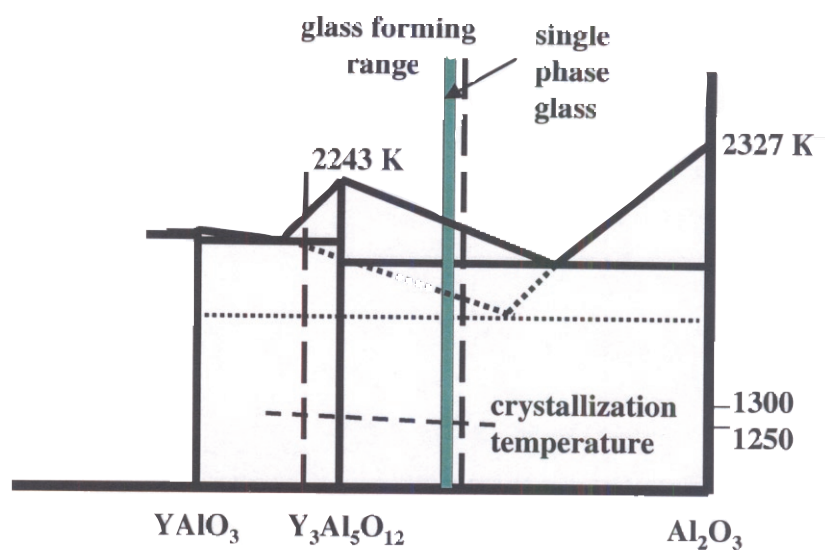


Figure 1. Schematic of the pseudo-binary Al_2O_3 - Y_2O_3 phase diagram showing the composition range studied in this work. The glass forming range, the region in which single-phase glass was formed, and the location of the metastable YAlO_3 - Al_2O_3 eutectic are marked. The dashed line indicates the temperature at which the liquid spontaneously crystallized in experiments where the cooling rate was not sufficient to form glass. The “glass forming range” is from 58-77 mole % aluminum oxide which were made into glass by containerless cooling of liquid at rates of up to 300 K/s. The glass forming range could be further extended by increasing the cooling rate.

2. X-ray and Neutron Structure Measurements on Glasses

X-ray and neutron techniques together provide detailed information about oxide glass structure. The strong scattering of X-rays by the high atomic number elements, such as yttrium and lanthanum, provides information about metal-metal correlations. Strong scattering of neutrons by oxygen provides details of the oxygen-oxygen correlations needed to analyze the bonding between the various M-O species present in the glass. This work was performed in collaboration with Dr. Chris Benmore at Argonne National Laboratory; use of the beam lines and the data analysis was supported by DOE.

Pulsed neutron diffraction measurements were made in single- and two-phase glasses using the Glass, Liquids and Amorphous Diffractometer (GLAD) at the Intense Pulsed Neutron Source. Approximately 1 gram samples of coarsely crushed glass were placed in thin-walled vanadium sample tubes and aligned with the neutron beam. Experiments were performed on two-phase $\text{Y}_3\text{Al}_5\text{O}_{12}$ -composition glass and single-phase AY-73 and $\text{La}_3\text{Al}_5\text{O}_{12}$ -composition glasses. Data acquisition times were 12 hours each for the glasses, background and calibration runs needed to reduce the data.

High energy X-ray diffraction was performed using a 1 mm square 100 keV beam at the BESSRC-CAT beamline ID-11-C at the Advanced Photon Source. Crushed glass samples were held in a cell consisting of two thin Mylar windows fixed to an aluminum holder. Data acquisition times were on the order of one hour. Background scattering measurements were made on the empty sample containment cell.

Figure 2 presents the radial distribution functions for a two-phase YAG-composition glass obtained using neutron and high energy X-ray diffraction techniques.

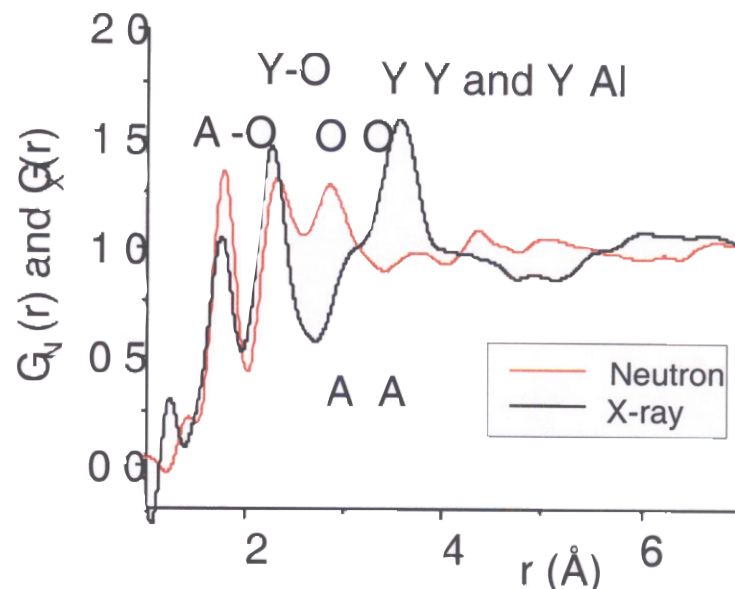


Figure 2. Radial distribution function for a two-phase YAG-composition glass obtained by pulsed neutron and high energy X-ray diffraction. Several of the correlations determined from the measurements are marked on the function. Note that the neutron data reveal O-O correlations and the X-ray data reveal Y-Y and Y-Al correlations.

3. Modelling of the Glass Structure

The reverse Monte Carlo simulation method was used to model the partial structure factor contributions using the neutron and X-ray data as constraints. The simulations employed a cubic box containing 3000 atoms using the exact composition ratio and atomic number density as measured in the glass samples. The simulations on the three glasses were performed in an identical manner so that the results could be directly compared to evaluate trends in the different glass structures. The main conclusions of the structure simulations are that the phase transition proceeds by a combination of changes in coordination number and bonding of the M-O polyhedra⁴.

The metal-oxygen stoichiometry is maintained in the glasses by complementary reactions which produce or consume oxygen. For example, transition from 7- to 6-coordinate Y-O produces an O²⁻ ion. A change from edge- to corner-shared connectivity between two polyhedra consumes an O²⁻ ion. The model is being refined to establish a detailed understanding of the glass and liquid structures.

4. ²⁷Al NMR Measurements

The coordination environment of Al³⁺ ions in alumina-yttria composition the glass was studied using ²⁷Al magic angle spinning NMR in collaboration with Dr. Brian Phillips at SUNY Stony Brook. The NMR results show that the glasses contain predominantly 4-coordinate Al³⁺ ions with populations of 5- and 6-coordinate ions detected in samples compositions from across the glass forming range^{5,6}. Work is in progress to refine analysis of the NMR data and study the structure of heat treated glasses.

5. Thermal Analysis

Preliminary thermal analysis experiments were performed on several glasses in experiments performed by Dr. Chandra Ray at University of Missouri-Rolla. Bulk glasses containing 24-40 molar % yttrium oxide were analyzed using Differential Scanning Calorimetry (DSC) at the University of California at Davis.

Analysis of the calorimetric data shows a strong glass transition (T_g) onset at temperatures from 1146-1156 K⁷. Values of T_g were insensitive to the glass composition. The glass transition was accompanied by a large change in heat capacity, ~ 80 J/g.f.w.K, as the glass structure relaxes. The onset of crystallization occurred at 1195-1224 K. Compositions containing 73.5 to 76 mole % alumina showed two exothermic events at temperatures separated by approximately 30 K.

In recent experiments, two-phase glasses containing 76 mole % alumina were heated to a temperature slightly above the first exothermic event in a DSC instrument and recovered for analysis. X-ray diffraction showed that despite the strong exotherm no crystals were present in the material. Experiments are in progress to establish the structural differences between the two glasses. The use of a DSC to investigate the glass-glass transition provides a means to investigate the thermodynamics of the phase transition.

6. ESL Experiments

Electrostatic levitation of YAG-composition samples was investigated using a high pressure ESL system which was developed at NASDA Tsukuba Space Center⁸. Experiments were performed at a pressure of 4 atm. in UHP nitrogen. Prior experiments performed in November, 2000 established conditions for levitation of molten calcium aluminate at temperatures up to about 2000 K⁹. Experiments performed in April, 2002 established conditions for levitation of YAG-composition liquids and obtained preliminary measurements of liquid density.

Samples for levitation were placed on an aerodynamic diffuser which prevented contact between the sample and the metal pedestal used to insert samples into the levitation electrode gap. The sample was positively charged by heating it with a CO₂ laser beam to a temperature where thermionic emission occurred. Stable levitation of samples *ca.* 1.8 mm in diameter was routinely achieved. Levitated samples could be cooled, vitrified, crystallized and remelted without loss of levitation stability. A backlit image of the levitated sample was used to obtain data on the density of the liquid over a temperature range 1470 to 2420 K¹⁰. Further experiments are being planned using the pressurized ESL and in the NASA ESL facility at Marshall Space Flight Center¹¹.

Planned Activities

Plans for the ongoing research are outlined below.

Investigation of transition kinetics by thermal processing of liquids and glasses. This work will build on the DSC annealing experiments in which a glass-glass transition can be accessed.

Studies of liquid properties. Measurements of liquid viscosity are a high priority to establish correlation with structure and the onset of the phase transition. Viscosity measurements obtained from fiber pulling experiments are subject to effects of high shear rates which occur in the liquids. Further ESL experiments to investigate liquid drop oscillation methods for measurement of viscosity are planned.

Work is continuing to enhance structural models using X-ray, neutron, NMR and in progress Raman studies of the glasses. The goal is to develop a detailed model of the glasses and liquids to determine effects of changes in coordination and connectivity.

The ground-based experiments are providing a sharp focus to the requirements of low gravity experiments needed to measure the kinetics of the L-L transition in diffusion-limited transport conditions and obtain accurate measurements of melt viscosity.

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RESIDUAL GAS EFFECTS ON DETACHED SOLIDIFICATION IN MICROGRAVITY

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Many microgravity directional solidification experiments yielded ingots with portions that grew without contacting the ampoule wall, leading to greatly improved crystallographic perfection [1]. Our long-term goal is to make such detached solidification reproducible, which requires a full understanding of the mechanisms underlying it. Our Moving Meniscus Model of steady-state detachment predicts that it depends strongly on the surface tension of the melt and the advancing contact angle with the ampoule wall [2-7]. Detached solidification is more likely when the contact angle for the melt on the ampoule wall is high, i.e. non-wetting. It has been claimed that impurities increase the contact angle. The objective of the current project is to determine the influence of residual gases on the surface tension and contact angle of molten semiconductors on typical ampoule materials. We are focusing on determining the influence of oxygen on the contact angle of molten InSb on clean silica ("quartz"), including the advancing and retreating contact angles in addition to the usual "equilibrium" contact angle.

We have created a gas flow system that allows us to control the oxygen partial pressure over a sessile drop of InSb on a horizontal quartz surface. The cell is slowly tilted while videotaping to reveal the contact angles on the two sides of the drop just prior to it rolling down the surface. Thus far, we have learned the following:

- Molten InSb readily forms an oxide layer in the presence of the trace amounts of oxygen found in high purity argon.
- This oxide contains a substantial amount of Ga, which presumably is a trace contaminant that is not detectable in the starting material.
- The addition of 10% hydrogen to the argon gas is sufficient to reduce the oxide and produce a clean drop.
- An infrared filter must precede the video camera in order to produce a sharp image of the drop for later image analysis.
- Tilting the surface on which the drop rests causes the two sides of the drop to display different contact angles, reflecting contact line sticking.
- Vibration strongly accelerates the approach of the drop to its final shape on a horizontal surface by helping to overcome sticking of the contact line.
- Oscillation of the drop surface due to vibration appears to increase as the surface is inclined from horizontal. Presumably, the angle at which the drop rolls down the surface is also reduced by vibration. This observation is particularly significant, as the meniscus must move along the ampoule wall during detached solidification.

Keywords: indium antimonide, detached solidification, contact angle

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Originally we had proposed to use the sessile drop technique in a closed cell, similar to that used here previously [8-10] but with the addition of a stabilized zirconia electrochemical oxygen pump and sensor. Upon thorough investigation, however, we discovered several difficulties with this approach: the operating temperature of zirconia cells is above the melting point of InSb; they are not available off-the-shelf in the form needed; and they are difficult to attach to the cell in a manner that withstand the elevated temperature required. For these reasons, we decided to flow a gas with known oxygen concentration through the cell.

Figure 1 shows a schematic diagram of the experimental apparatus. To perform an experiment, a piece of InSb was loaded into the experiment cell, which was connected to the gas supply system. The furnace was heated until the InSb melted. In early experiments, the melt appeared to have some oxide on its surface. This oxide was slowly reduced by passing argon containing 10% hydrogen over it. In the presence of high purity argon alone, the oxide slowly reformed. Reportedly, this argon contained on the order of 1 ppm of oxygen. After cooling the furnace, the frozen drops were removed and examined by scanning electron microscopy. Some were cleaved and the cross sections viewed, as illustrated in Figure 2. Figure 3 is an energy dispersive x-ray spectrum of oxide, showing a strong Ga peak that was not present on either the starting material or on unoxidized drops. Apparently gallium was preferentially oxidized, presumably because its oxide has a higher free energy of formation (more negative) than does indium oxide.

Drops were videotaped during an experiment. Frames were later grabbed and analyzed using using HL++ 98 image analysis software. Figure 4 shows a sessile drop of unoxidized InSb on a quartz microscopic slide with 90%Ar - 10%H₂ flowing through the cell throughout the experiment. These frames show that the contact angle was relatively constant and significantly higher than the 112° measured under “static vacuum” by Harter *et al.* [11].

In order to fully achieve the objectives of this project, we must determine the contact angle versus oxygen fugacity (or partial pressure) in the gas phase above the melt. Thus, we must know this fugacity and be able to control it. In order to vary the oxygen fugacity, we will mix argon containing a known amount of hydrogen with argon containing a known amount of oxygen. From the well-established reaction kinetics of hydrogen and oxygen, we have determined that the residence time in the experiment cell is sufficient to assure that equilibrium is reached at 530°C (see Figure 5). The equilibrium conversion can readily be calculated from the free energy of formation of water at that temperature. In order to be certain that we know the oxygen fugacity thus achieved, we are installing an oxygen sensor in the effluent gas stream.

Acknowledgement

The InSb used for these experiments was kindly donated by Firebird Semiconductors Ltd., Trail, BC, Canada V1R 2T3.

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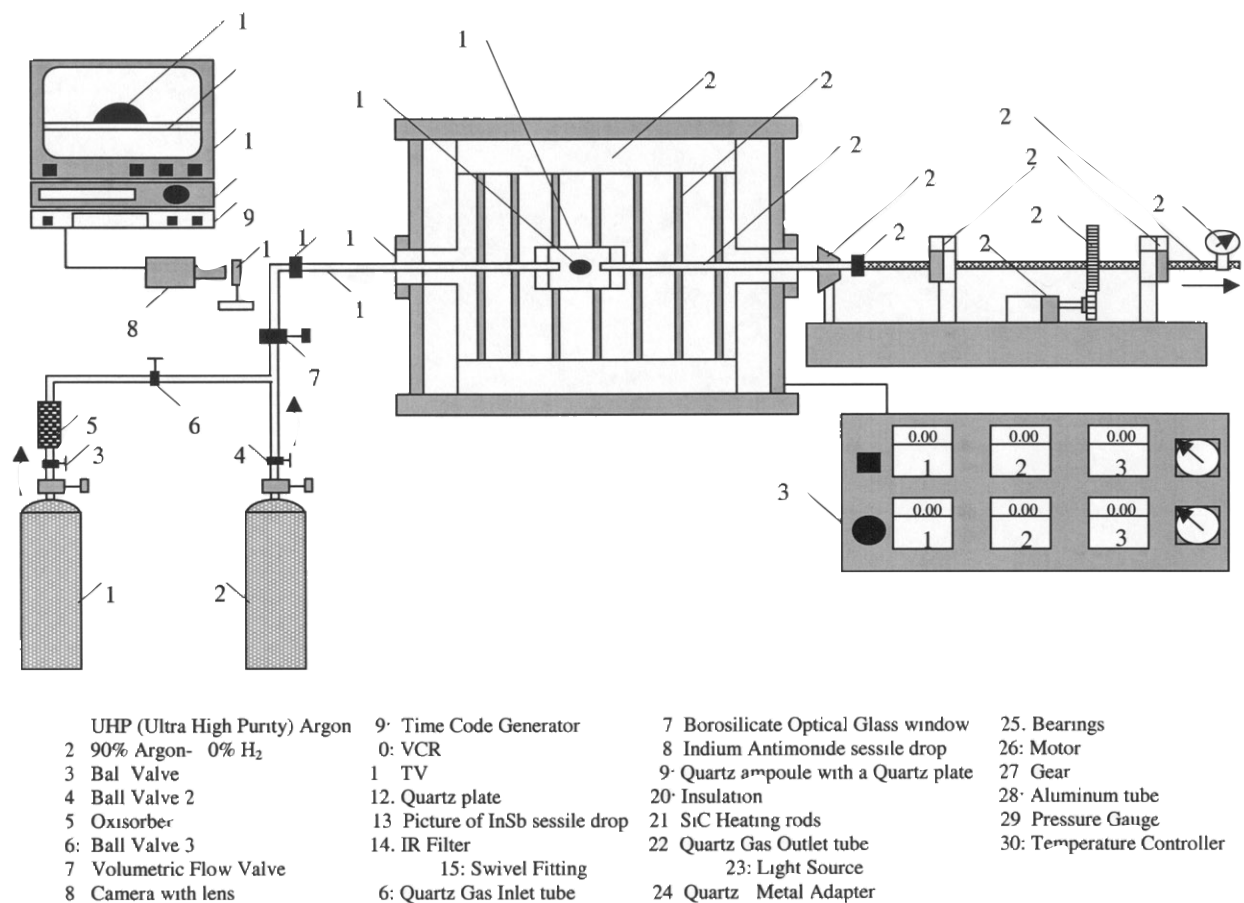


Figure 1 Schematic diagram of apparatus

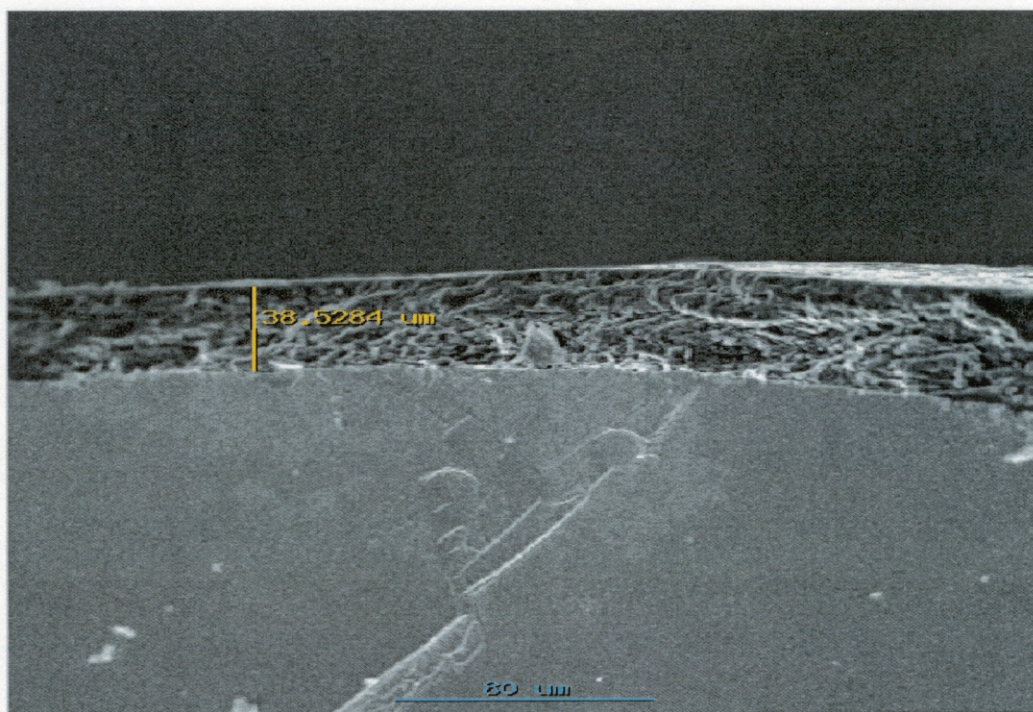
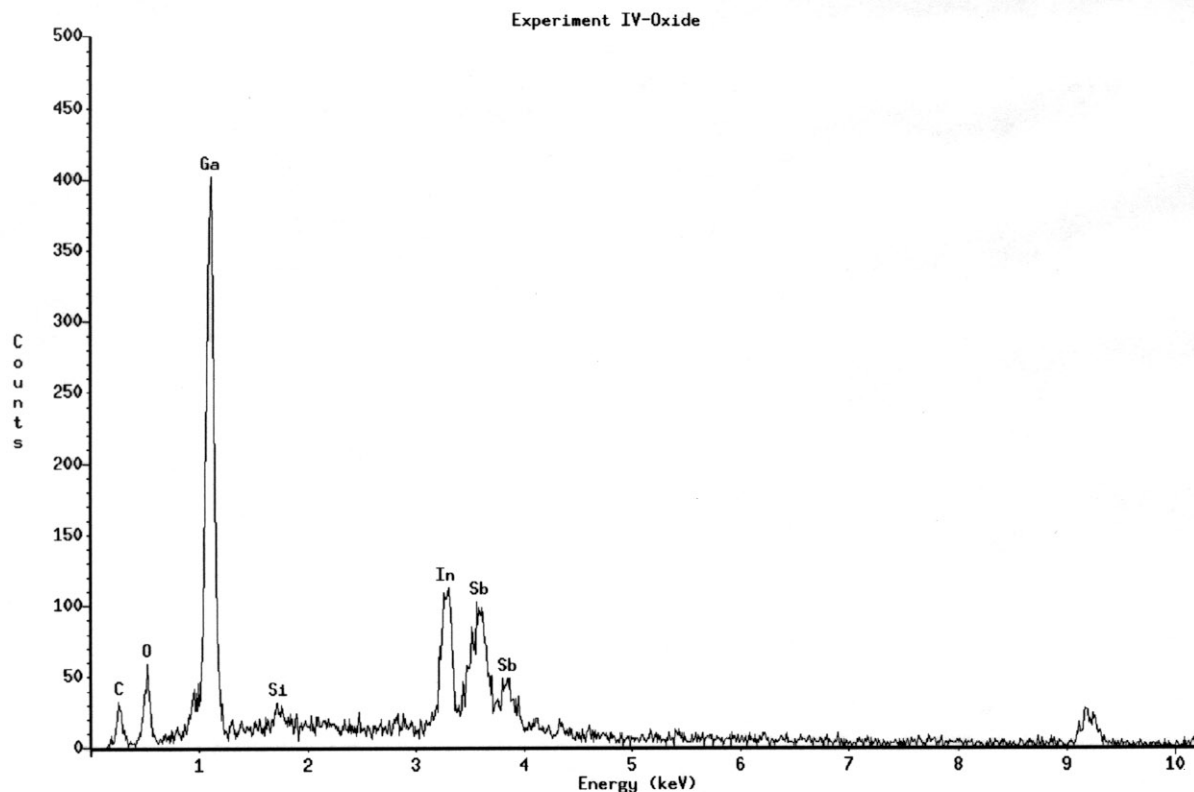


Figure 2. Cleaved cross section of frozen drop showing oxide layer of thickness $\sim 38 \mu\text{m}$.
Magnification: 270X



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Experiment IV-Oxide
Column       : JEOL,Pioneer
Take-off angle : 30
Acquisition type : eds
Creation time  : 2001/12/14 1:46
Livetime      : 13
Deadtime      : 4.49
Channels      : 1024
Channel width  : 10
Detector type  : Silicon/Lithium
Window type   : norvar
Window thickness : 0.3
Coating material : Al
Coating thickness : 0.04
Contact material : Au
Contact thickness : 0.02
Crystal thickness : 3

Accelerating voltage : 15
Magnification        : 1300
Charge               : 13
Beam current         : 1
Beam spot size       : 0
Beam location        : 0.0
Working distance     : 15
Stage X              : 0
Stage Y              : 0
Stage Z              : 0
Stage tilt           : 0
Stage rotation       : 0
Contamination material : none
Contamination thickness : 0

```

File name :

Notes:

Fri Dec 14 01:46:12 2001

Experiment IV-Oxide

Livetime : 13.0 Sec.

Technique: Least Squares Fit

Elements Present:
C(6), O(8), Ga(31), Si(14), In(49),
Sb(51)

Energy (keV)	Intensity (counts)	Elements Present
0.267	183	C Ka
0.523	337	O Ka

Figure 3. Energy-dispersive x-ray spectrum of oxidized InSb drop.

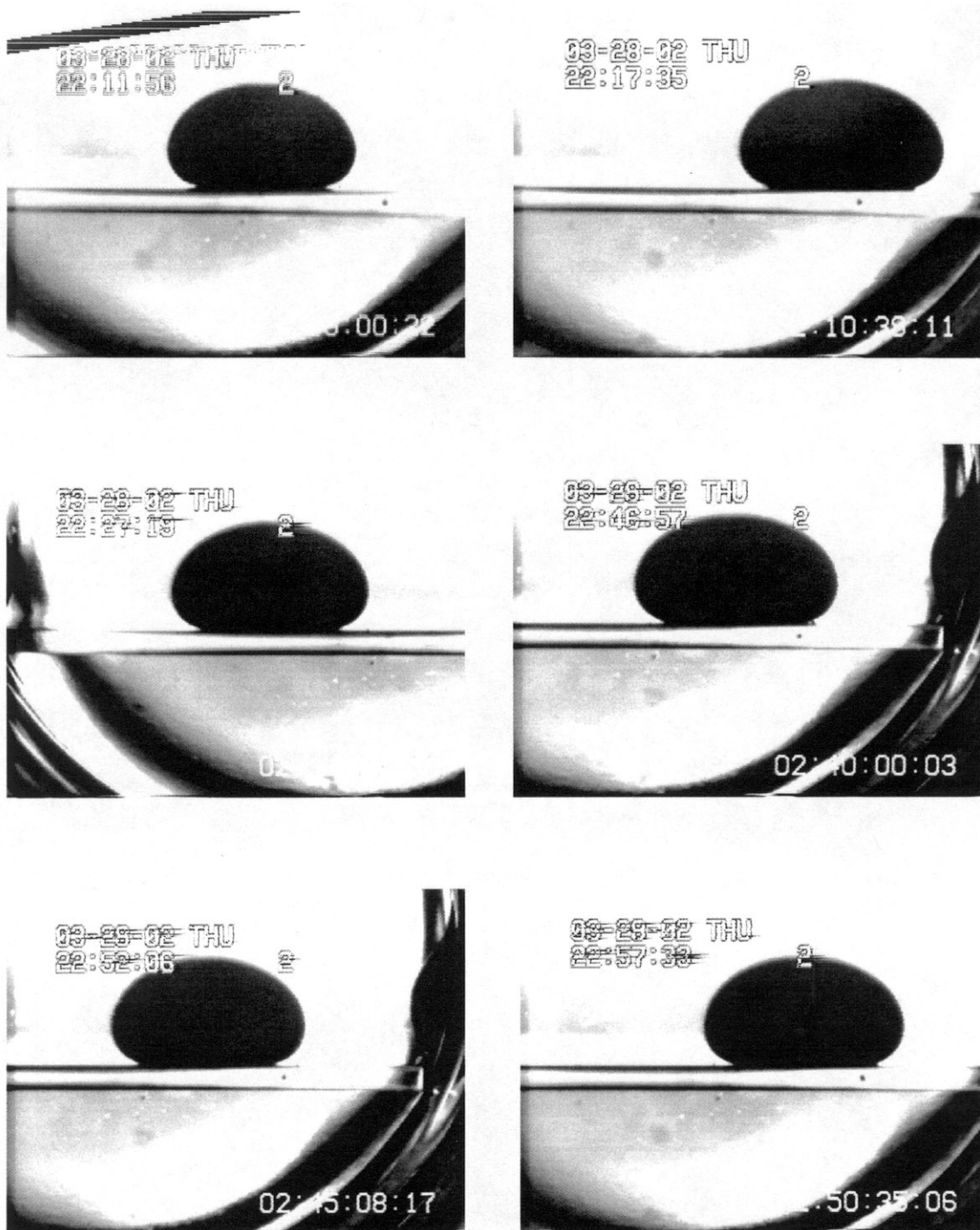


Figure 4. Sessile drop during an experiment in the presence of 90%Ar-10%H₂.

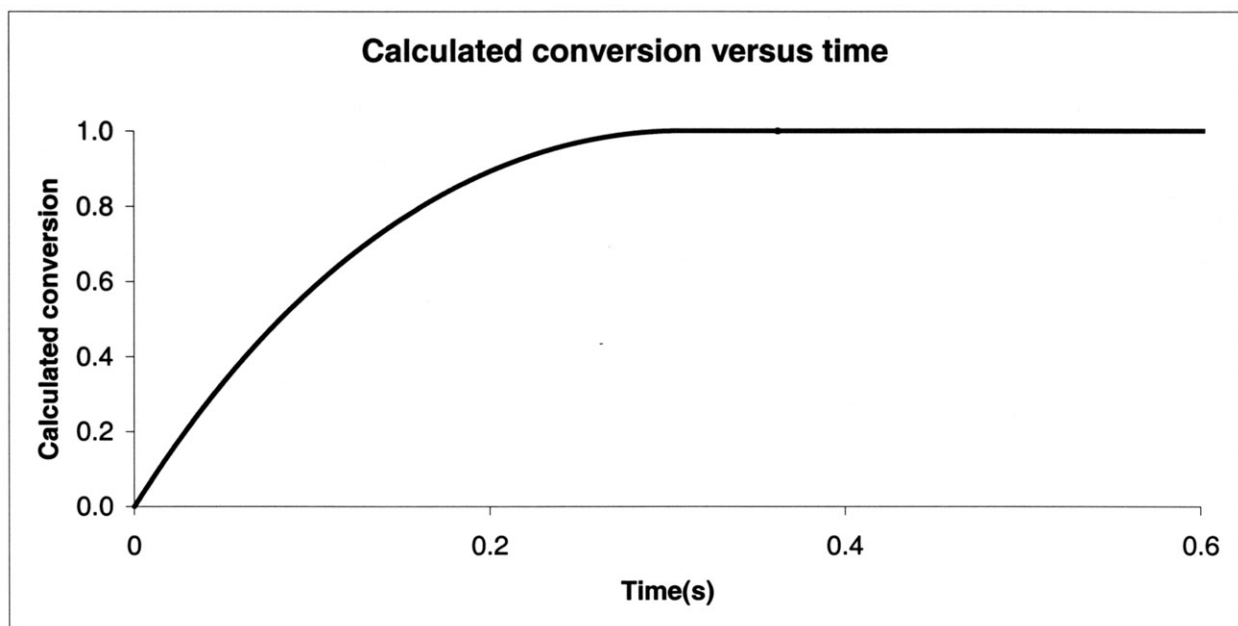


Figure 5. Calculated conversion of hydrogen to water by reaction with oxygen at 530°C.
The residence time in the experiment cell is 2.4 s.

MELT FLOW CONTROL IN THE DIRECTIONAL SOLIDIFICATION OF BINARY ALLOYS

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Our main project objectives are to develop computational techniques based on inverse problem theory that can be used to design directional solidification processes that lead to desired temperature gradient and growth conditions at the freezing front at various levels of gravity. It is known that control of these conditions plays a significant role in the selection of the form and scale of the obtained solidification microstructures.

Emphasis is given on the control of the effects of various melt flow mechanisms on the local to the solidification front conditions. The thermal boundary conditions (furnace design) as well as the magnitude and direction of an externally applied magnetic field are the main design variables. We will highlight computational design models for sharp front solidification models and briefly discuss work in progress toward the development of design techniques for multi-phase volume-averaging based solidification models.

Model Description

Let us introduce a model directional solidification problem of a dilute, incompressible, electrically conducting binary alloy in a two-dimensional rectangular enclosure with an open boundary (Fig. 1). At time $t = 0^+$, a cooling heat flux is applied on the mold boundary Γ_{OS} and solidification commences. Here, we assume a-priori that the growth conditions are such that solidification occurs with a stable solid-liquid interface [1]. This model provides us with the opportunity to concentrate on the melt flow mechanisms and in addition to control interface quantities that are readily available in the direct analysis.

In the following problem definition, the following dimensionless numbers are used [1], [2]: θ (dimensionless temperature) $\equiv (T - T_o)/\Delta T$, Ha (Hartmann number), Le (Lewis number), Ma_T (thermal Marangoni number), Ra_T (thermal Rayleigh number), Ra_c (solutal Rayleigh number), R_α (ratio of thermal diffusivities), R_k (ratio of thermal conductivities) and Ste (Stefan number). The equations governing the various transport mechanisms in the melt in the binary alloy solidification system are

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + Pr \nabla^2 \mathbf{v} - [Ra_T Pr, \mathbf{i} - Ra_c Pr c] \mathbf{e}_g + Ha^2 Pr [\mathbf{v} \times \mathbf{e}_B] \times \mathbf{e}_B \quad (1)$$

$$\frac{\partial, \mathbf{i}}{\partial t} + \mathbf{v} \cdot \nabla, \mathbf{i} = \nabla^2, \mathbf{i} \quad (2)$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = Le^{-1} \nabla^2 c \quad (3)$$

Keywords: computational design, solidification control, inverse problems, fluid flow control, new research

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The thermal field distribution in the solid is governed by the heat conduction equation:

$$\frac{\partial_s}{\partial t} = R_\alpha \nabla^2_{,s} \quad (4)$$

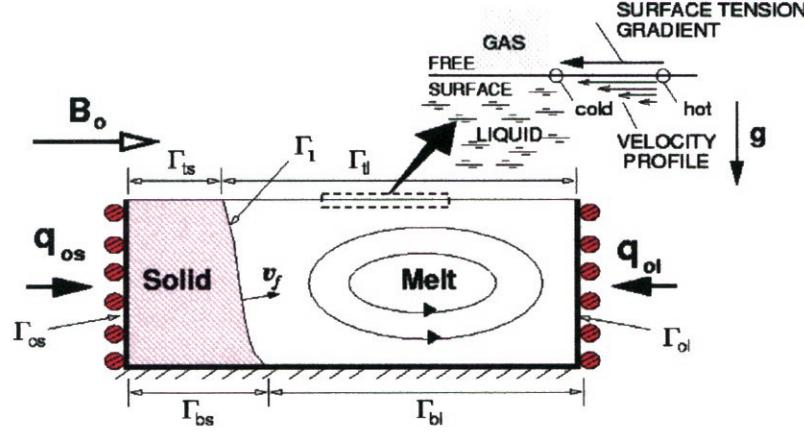


Figure 1: Schematic of the binary alloy solidification problem in an open boat configuration under the influence of an externally applied magnetic field.

The interfacial temperature is determined by the equilibrium phase diagram:

$$\theta = \theta_m + mc \quad (5)$$

where the dimensionless slope m of the liquidus is given as $m = m_{\text{liquidus}} \Delta c / \Delta T$, m_{liquidus} is the dimensional slope of the liquidus and θ_m is the dimensionless melting temperature.

The interfacial thermal and solute fluxes are governed by the Stefan condition and the solute conservation condition on the freezing interface:

$$R_k \frac{\partial_s}{\partial n} - \frac{\partial_{,l}}{\partial n} = Ste^{-1} \mathbf{v}_f \cdot \mathbf{n} \quad (6)$$

$$\frac{\partial c}{\partial n} = Le(c_0 - 1) \mathbf{v}_f \cdot \mathbf{n} (c + \delta) \quad (7)$$

where the normal vector $\mathbf{n}$ is pointing out from the liquid domain, κ is the partition coefficient and $\delta \equiv c_0 / \Delta c$ is the ratio of the reference concentration c_0 and reference concentration drop Δc .

No-slip and no-penetration boundary conditions are imposed on all surfaces other than the upper free surface. The hydrodynamic condition on Γ_{tl} is of the form:

$$\nabla(\mathbf{v} \cdot \mathbf{t}) \cdot \mathbf{n} = Ma_T (\nabla_{,l} \cdot \mathbf{t}) \quad (8)$$

where $\mathbf{t}$, is a tangent vector to the free-surface. Insulating thermal boundary conditions are imposed on the top and bottom boundaries of the solid and liquid domains. Thermal boundary conditions are provided on Γ_{os} and Γ_{ol} . Finally, a solute impermeable condition is imposed on the mold boundaries and the free surface.

The solution scheme implemented uses a front-tracking SUPG/PSPG finite element method with mass lumping and preconditioning [1].

Reference Design And Parametric Studies

Before we address computational design solidification problems, it is imperative to provide an understanding of the effects of the various physical mechanisms on the local to the freezing front conditions. A parametric study was performed in this context to investigate the effects of various process parameters.

Let us consider a rectangular cavity with an open free surface of dimensions 2 cm x1 cm initially filled with molten antimony-doped germanium at 40°C overhead (Fig. 1). The wall Γ_{ol} is maintained at the initial temperature, while Γ_{os} is suddenly cooled to a temperature 40°C below the melting temperature of pure germanium and maintained at that temperature for $t > 0$. The thermophysical properties are extracted from [1].

At $t=0^+$ solidification starts and takes place under standard laboratory conditions. We refer to this problem as the *reference design problem*. The results of the *reference design problem* at $\tau = 10$ are shown on the left of Fig. 2.

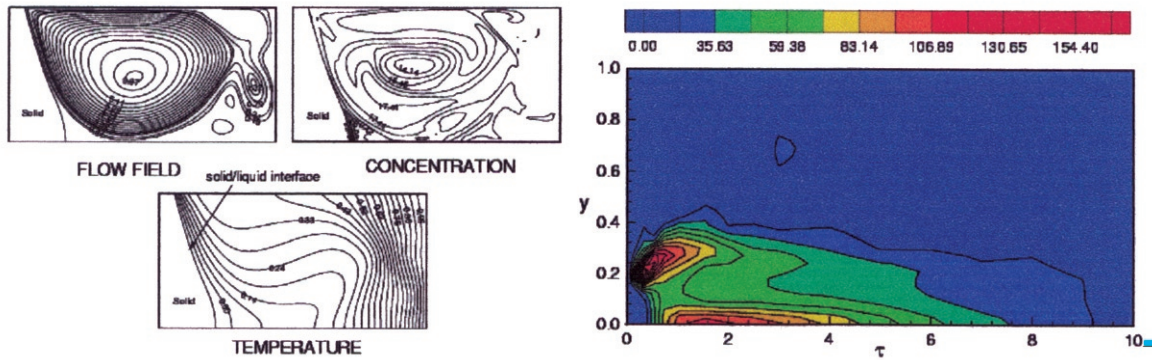


Figure 2: Normal gravity and zero magnetic field conditions for the solidification of SbGe. On the left: Contours of stream function, solute concentration and temperature fields at time $\tau = 10$. On the right: Calculated history of the solid-liquid interface concentration during the entire simulation.

Figure 2 also presents the history of the concentration on Γ_l during the entire simulation. This plot effectively shows the pattern of the solute variation obtained in the final solid. To assess the relative importance of thermocapillary versus buoyancy effects on solidification, a calculation was performed for solidification in a very low-gravity $g=10^{-5} g_{\text{earth}}$ environment (Fig. 3) At early times $\tau < 0.5$, thermal gradients on the free surface lead to surface-tension gradients and a thermocapillary flow develops slowly, forming a small counter-clockwise cell around the free surface very close to Γ_l . There is almost no convection in the lower part of the cavity at this time. As the solidification proceeds further, the strength of this recirculating fluid flow slowly increases, along with a steady increase in the size of the cell. Around $\tau = 2$, the main recirculating cell fills almost the entire cavity. At the same time, a secondary cell pattern forms at the right end of the cavity. After around $\tau = 3$ there is almost no change in the structure of the main cell, even though its strength steadily increases with time (Fig. 3 (left)).

This complex evolution of the melt flow has significant impact on various solidification parameters (e.g. compare Figs. 2 (right) and 3 (right)) [1].

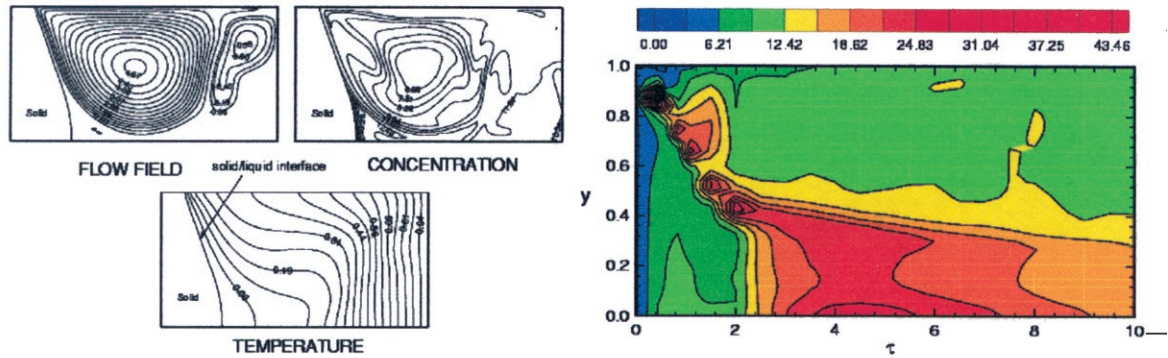


Figure 3: Reduced gravity ($g=10^{-5} g_{\text{earth}}$) conditions and zero magnetic field for the solidification of SbGe. On the left: Calculated contours of stream function, solute concentration and temperature fields at time $\tau = 10$. Notice the significant influence of the flow field on the solute distribution in the melt. On the right: Calculated history of the solid-liquid interface concentration during the entire simulation.

An extensive series of simulations were conducted under various levels of gravity (Fig. 4). These studies have shown that ‘flat interface growth’ cannot be achieved by a reduced gravity environment and additional means of control are needed. Simulations were also conducted at various inclinations of the magnetic field. Figure 5 shows the variety of flow patterns obtained for various magnetic field inclinations at time $\tau = 10$. The prominent effect of varying the orientation of the magnetic field is to drastically alter the structure of the fluid flow especially under reduced gravity conditions.

Finally, Figure 6 illustrates the variety of melt flow patterns obtained by varying the strength of the applied horizontal magnetic field under normal and reduced gravity conditions. An increasing magnetic field damps the melt flow and also has significant impact on the structure of the flow and application of sufficiently high magnetic fields (Fig. 6(c)) leads to separation of the thermocapillary- and buoyancy-driven rolls. As one can note from Fig. 6(f), solidification under reduced gravity and sufficiently strong magnetic field ensures that the solid-liquid interface is almost flat which in fact is one of the objectives of the design problems under consideration. In the following section, we will briefly highlight a design methodology to achieve a desired flat-interface growth that is also ensured to be morphologically stable.

In closure, Fig. 7 compares the solute pattern obtained under normal and reduced gravity conditions with an applied magnetic field. As expected, markedly different transport patterns in the two systems lead to entirely different form of solute segregation. As seen in Fig. 7(a), the maximum solute concentration under normal gravity conditions is seen in the bottom part of the rectangular cavity at very early times. In contrast, Fig. 7(b) shows that the maximum solute collection occurs very near the free-surface and at early times. This trend is in conformity with the fluid flow circulation which is restricted mainly to regions close to the free-surface.

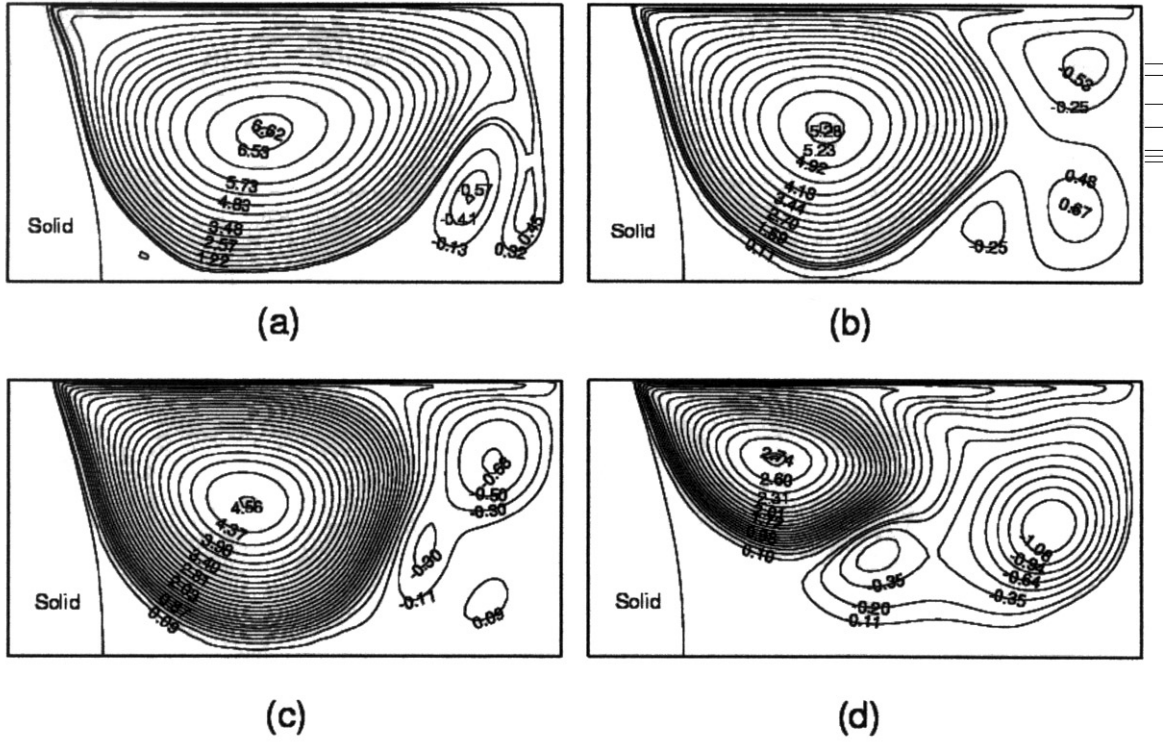


Figure 4: Effects of gravity with no magnetic field: Contours of stream function at time $\tau = 5$ for the solidification of SbGe under varying levels of gravity: (a) $0.5g_{\text{earth}}$ (b) $0.1g_{\text{earth}}$ (c) $0.01g_{\text{earth}}$ (d) $10^{-5}g_{\text{earth}}$.

Inverse Design To Achieve A Desired Stable Growth

Using parametric studies to compute the optimal process conditions becomes an expensive and time-demanding process. To alleviate such difficulties, a computational design framework was developed for the thermal design of directional solidification processes. The objective here is to control the mold wall cooling/heating boundary conditions in order to achieve a desired stable interface growth. As a first attempt, the magnitude and orientation of the magnetic field and gravity are a-priori selected based on the parametric studies discussed earlier.

To simplify the design analysis presented here, we assume eutectic solidification with the interfacial temperature of the liquid and solid and composition of the liquid given by

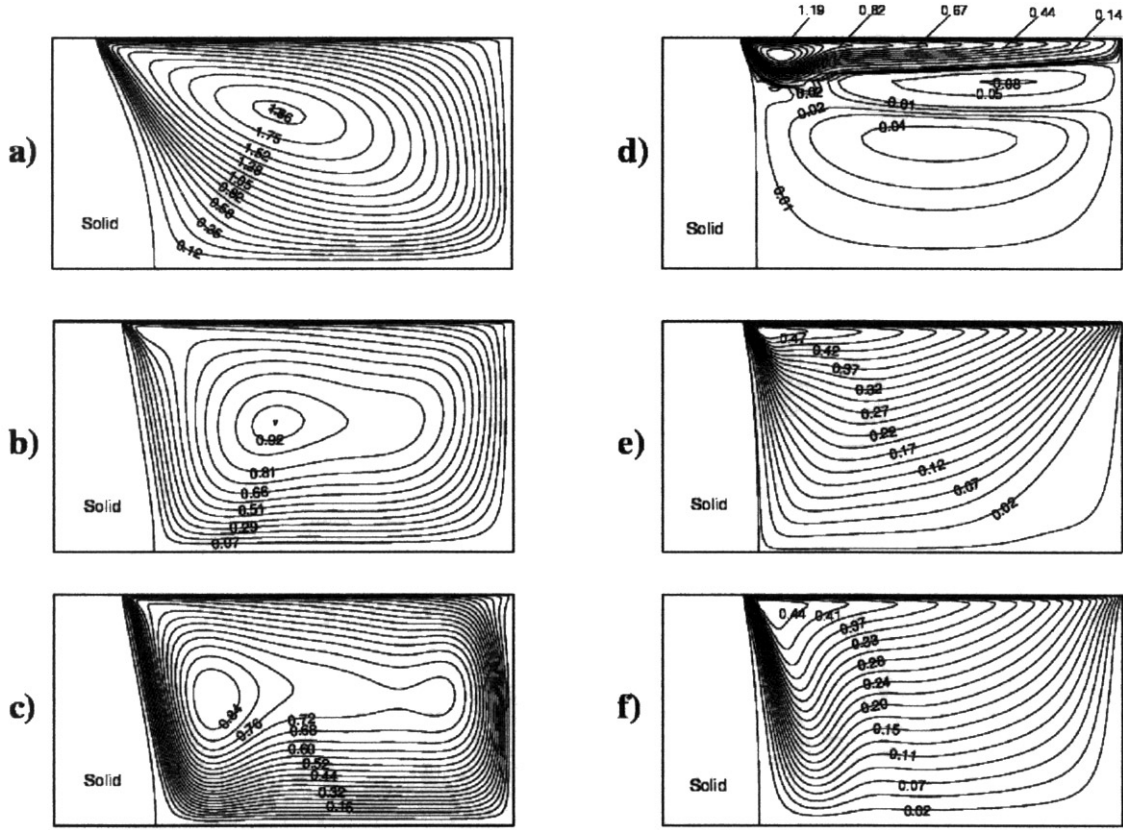
$$\theta_l = \theta_s = \theta_E \quad \text{and} \quad c = c_E \quad \text{on} \quad \Gamma_I(t) \quad (9)$$

The solid composition is determined by the dimensionless mass balance

$$(c_s - c_E)(\mathbf{v}_f \cdot \mathbf{n}) = Le^{-1} \frac{\partial c}{\partial n} \quad (10)$$

With all remaining governing equations as given earlier, we pose the following inverse design problem (see Fig. 8):

Find the cooling heat flux $q_{os}(\mathbf{x}, t)$ on the boundary Γ_{os} as well as the heat flux condition $q_{ol}(\mathbf{x}, t)$ on the vertical mold wall Γ_{ol} (see Fig. 8a) so that in the presence of coupled thermocapillary, buoyancy and electromagnetically driven convection in the melt, a desired flat-interface growth (with desired flux G and growth velocity $\mathbf{v}_f$) is achieved that is ensured to be morphologically stable.



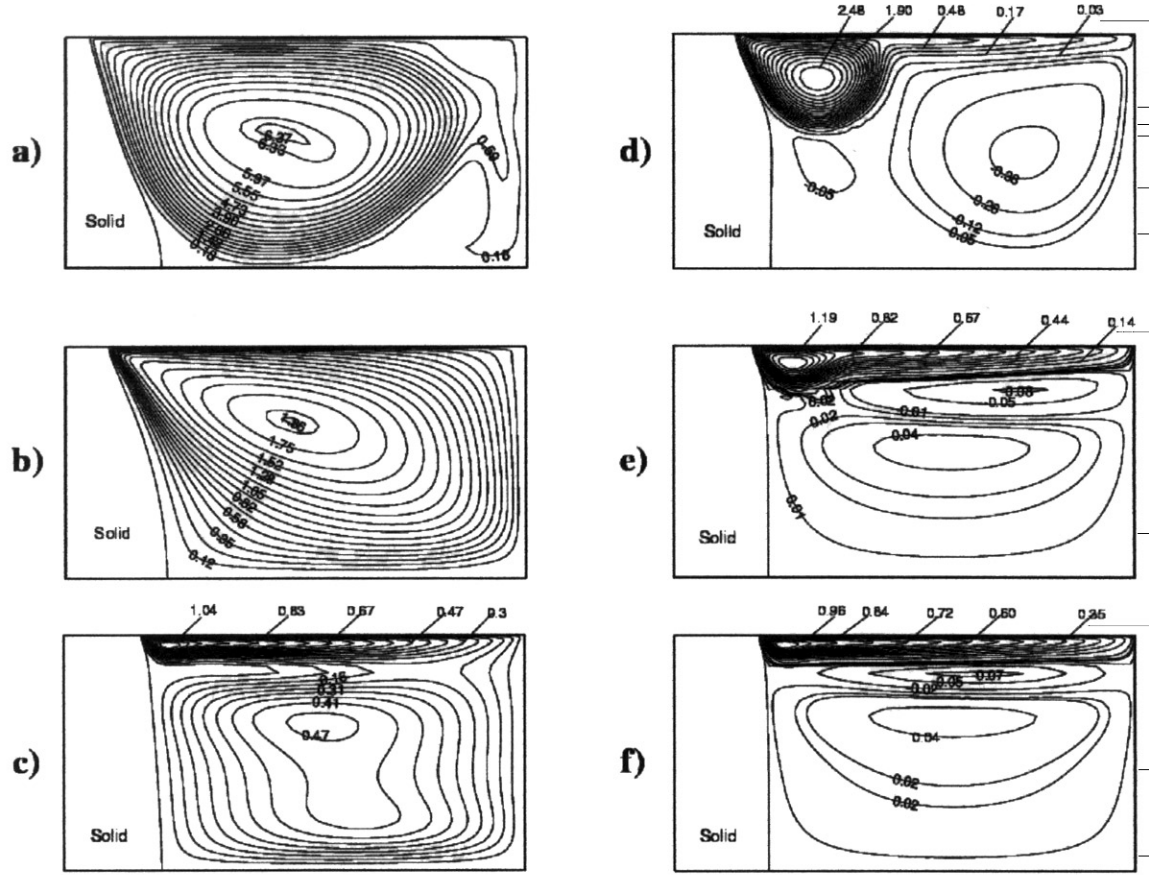


Figure 6: Effect of the magnetic field strength: Calculated contours of stream function at time $\tau = 10$ for the solidification of SbGe. Solidification under normal gravity conditions: (a) $Ha=10$ (b) $Ha=100$ (c) $Ha=200$, Growth under reduced gravity ($g = 10^{-5}g_{\text{earth}}$) conditions: (d) $Ha=10$ (e) $Ha=100$ (f) $Ha=200$.

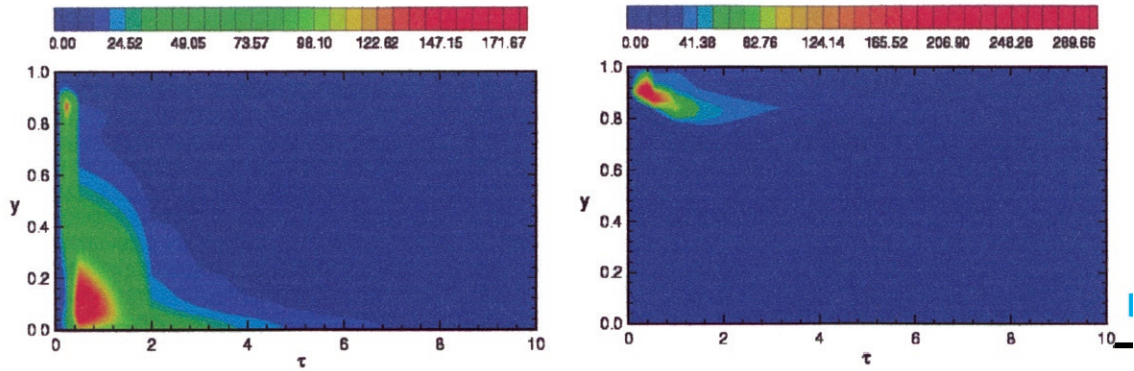


Figure 7: History of the solid-liquid interface concentration during the entire simulation of SbGe solidification for $Ha=100$: (a) normal gravity conditions; (b) reduced gravity ($g=10^{-5}g_{\text{earth}}$) conditions.

to be sufficient to ensure stability of the solid-liquid interface. We herein enforce stability by explicitly choosing an interface thermal gradient G and growth velocity $\mathbf{v}_f$ such that $G/|\mathbf{v}_f|$ marginally satisfies the constraint given in equation (11). In our preliminary work, we have chosen $\mathbf{v}_f$ as the growth corresponding to diffusion based process [4].

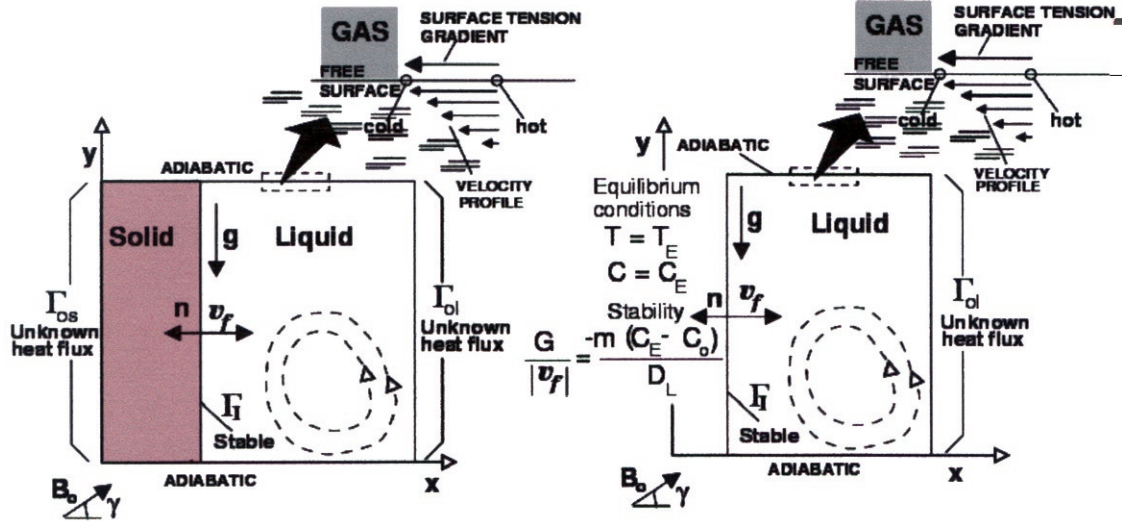


Figure 8: Definition of the design eutectic solidification problem. The design objectives are the achievement of a desired growth v_f under the conditions of marginal stability.

In the following discussion, we present the essentials of the adjoint method for solving the above described inverse design eutectic solidification problem. The space of *admissible controls* is defined as the Hilbert space $\mathcal{U} = H^1(\Gamma_{ol} \times [0, t_{\max}])$. With a *guessed* heat flux $q_{ol}(\mathbf{x}, t)$, $(\mathbf{x}, t) \in \Gamma_{ol} \times [0, t_{\max}]$, one can define a direct coupled thermocapillary-buoyancy-electromagnetic convection problem on the prescribed domain $\Omega_l(t)$. Let us denote its solution for the temperature, concentration and flow fields as $\theta(\mathbf{x}, t; q_{ol})$, $c(\mathbf{x}, t; q_{ol})$ and $\mathbf{v}(\mathbf{x}, t; q_{ol})$, respectively. The equilibrium condition $\theta(\mathbf{x}, t) = \theta_E$, $(\mathbf{x}, t) \in \Gamma_l \times [0, t_{\max}]$ is not used in this *direct problem* definition, thus it is not guaranteed to be satisfied. For an arbitrary $q_{ol} \in H^1(\Gamma_{ol} \times [0, t_{\max}])$, we define a cost functional:

$$\mathcal{J}(q_{ol}) = \frac{1}{2} \|\theta(\mathbf{x}, t; q_{ol}) - \theta_E\|_{L_2(\Gamma_l \times [0, t_{\max}])}^2 + \frac{\gamma}{2} [\|q_{ol}\|_{L_2(\Gamma_{ol} \times [0, t_{\max}])}^2 + \|\nabla q_{ol}\|_{L_2(\Gamma_{ol} \times [0, t_{\max}])}^2] \quad (12)$$

where $\gamma \in \mathfrak{R}^+$ is an appropriate regularization parameter chosen based on the numerical errors in the algorithm. In this paper, our objective is to construct a minimizing sequence $q_{ol}^k(\mathbf{x}, t) \in \mathcal{U}$, that converges to at least a local minimum of $\mathcal{J}(q_{ol})$.

To perform the optimization procedure that minimizes $\mathcal{J}(q_{ol})$, we will need to define a *continuum sensitivity problem* in terms of the sensitivity velocity field $\hat{V}(\mathbf{x}, t; q_{ol})$, sensitivity temperature field $\hat{\Theta}(\mathbf{x}, t; q_{ol})$ and sensitivity concentration field $\hat{C}(\mathbf{x}, t; q_{ol})$. This linear problem is derived by computing the linear perturbations of the fields $\theta(\mathbf{x}, t; q_{ol})$, $c(\mathbf{x}, t; q_{ol})$ and $\mathbf{v}(\mathbf{x}, t; q_{ol})$, respectively, with respect to the variations $\Delta q_{ol}(\mathbf{x}, t)$ of the design heat flux q_{ol} [3]-[8]. In order to realize the minimization of $\mathcal{J}(q_{ol})$, it is essential to find its gradient $\mathcal{J}'(q_{ol})$ with respect to the design flux q_{ol} . An associated *adjoint problem* can be defined in terms of the adjoint velocity field $\hat{\phi}(\mathbf{x}, t; q_{ol})$, adjoint temperature field $\hat{\psi}(\mathbf{x}, t; q_{ol})$, and adjoint concentration field $\hat{\rho}(\mathbf{x}, t; q_{ol})$. The gradient of $\mathcal{J}(q_{ol})$ with respect to the scalar product $(\cdot, \cdot)_{H^1(\Gamma_{ol} \times [0, t_{\max}])} \equiv (\cdot, \cdot)_{L_2(\Gamma_{ol} \times [0, t_{\max}])} + (\nabla \cdot, \nabla \cdot)_{L_2(\Gamma_{ol} \times [0, t_{\max}])}$ was shown to be given by [5,6]

$$\mathcal{J}'(q_{ol}) = z + \gamma q_{ol} \quad (13)$$

where z is the solution of an additional variational equation on Γ_{ol} :

$$-\Delta z(x, t) + z(x, t) = \psi(x, t; q_{ol}) \quad (14)$$

Thus, to calculate the gradient of the cost functional including an H^1 type regularized formulation, the solution component $\tilde{\psi}(x, t; q_{ol})$ of the adjoint equations has to be first computed together with the solution z of the above variational problem.

After having obtained an analytical expression for the exact gradient, any of the standard functional minimization techniques can be used for solving the above defined optimization problem such as the non-linear conjugate gradient method (CGM) [6].

Numerical Example In The Design Of Eutectic Solidification

Consider a rectangular cavity with an open free surface of dimensions 20 mm x 20 mm filled with molten Sb - 8.6 wt% Ge, initially at 100°C above the eutectic temperature (592° C). At time $t = 0^+$, the left wall Γ_{os} is suddenly cooled to a temperature 100 °C below the eutectic temperature and maintained at that temperature for times $t > 0$. All other walls are insulated. The thermophysical properties are given in [4].

At $t = 0^+$ the freezing process starts and takes place under standard laboratory conditions. We refer to this problem as the *reference design problem*. In [4] it has been shown that the solution of this reference problem leads to a complex variation of solute in the product and in addition corresponds to a physically unrealistic (unstable) process. A design problem is thus introduced to compute the transient mold walls thermal conditions for the reference eutectic solidification system such that a stable growth is achieved with a growth velocity equal to that of a solidification problem controlled only by heat/solute diffusion. A horizontal magnetic field of $Ha = 36.74$ is applied. This design example computes process parameters that lead to “diffusion-based” conditions in the presence of convection. We pose the following problem:

Find the thermal boundary conditions on the left wall $\mathbf{x} = 0$ and the right wall $\mathbf{x} = 1$ such that with coupled thermocapillary, buoyancy, and electromagnetic convection in the melt, a vertical desired interface growth is achieved that is morphologically stable (see Fig. 8).

The inverse solidification problem can be decomposed into an *inverse heat conduction problem* in the solid and a *inverse convection problem* in the melt (Fig. 8). The inverse problem in the liquid domain solves for $q_{ol}(y, t)$ at $x = 1$ using the given freezing interface velocity $\mathbf{v}_f(t)$ and the interface thermal gradient G . $\mathbf{v}_f(t)$ is here defined by solving a direct solidification problem without the effects of melt convection and G is chosen using this interface velocity field such that the stability condition is marginally satisfied. An initial guess $q_{ol}^0(y, t) \equiv 0$ corresponding to the reference eutectic solidification problem was chosen to start the CGM algorithm. Within each CGM iteration, the direct, adjoint and sensitivity problems are solved using the same finite element algorithms [7].

The development of the heat flux profiles during the intermediate stages of CGM process is shown in Fig. 9. Note that this optimal heat flux profile $\bar{q}_{ol}(y, t)$ shows largest heating at very early times. This strong heating flux has to be applied at early times in order to counteract the effects of coupled thermocapillary and buoyancy-driven fluid flow at the very early stages of the solidification process. It is the combined application of the heat fluxes $\bar{q}_{os}(y, t)$ and $\bar{q}_{ol}(y, t)$, which leads to the desired stable growth conditions.

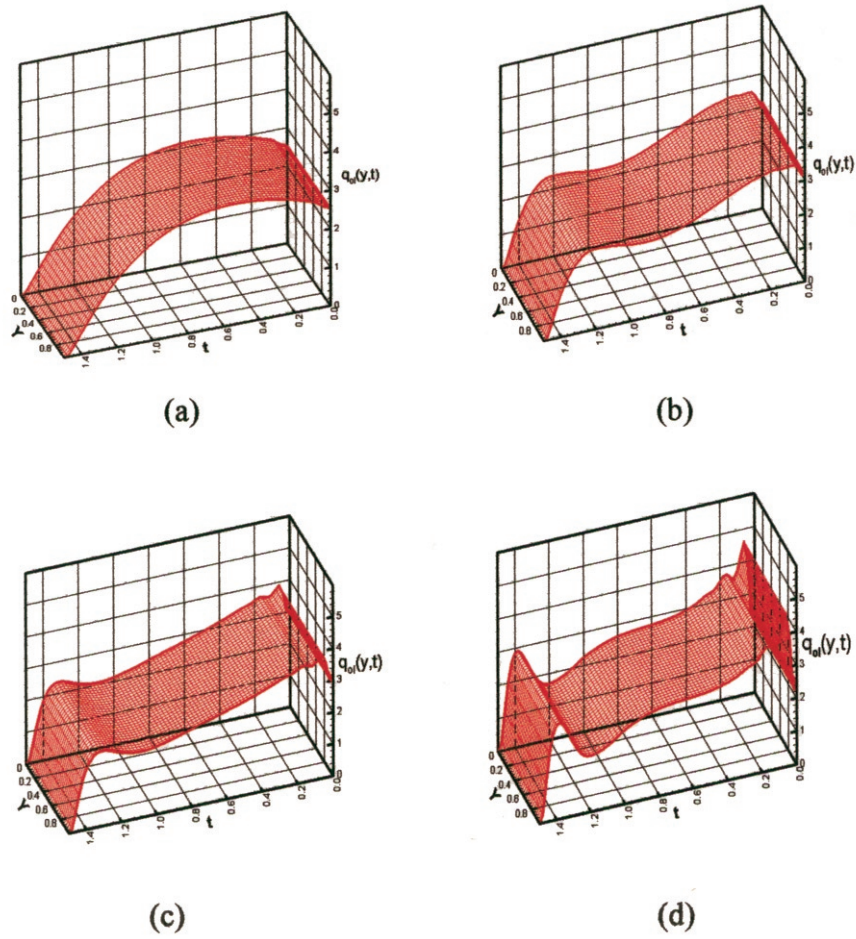


Figure 9: Flux distribution $q_{ol}^k(y, t)$ obtained at CGM iterations $k = 1, 2, 5$, and 10 , starting from an initial guess heat flux $q_{ol}^0(y, t) \equiv 0$. The solution at $k=10$ is nearly the final optimal solution.

We proceed to evaluate how close the desired design objectives have been met. A direct eutectic solidification problem is considered with the calculated optimal solid side flux $\bar{q}_{os}(y, t)$ applied on the left boundary $x = 0$ (not shown here) and the liquid side flux $\bar{q}_{ol}(y, t)$ applied on the right boundary $x = 1$. The top and bottom walls are, as before, insulated. We refer to this problem as the *optimal design eutectic-solidification problem*.

Representative transient temperature, concentration and flow fields corresponding to the optimal design problem are illustrated in Fig. 10. The strong heating flux on the right boundary $x = 1$ is necessary to overcome the solutal undercooling and maintain a stable interface growth throughout the process. Figure 11(b) shows the dimensionless contours of $\Delta(y, t) \equiv G/|\mathbf{v}_f| + m(C_E - C_o)/D_L$ as a function of the y -coordinate and time. Stable growth ($\Delta(y, t) \geq 0$) is achieved for the entire duration of solidification confirming the realization of the design objectives. Finally, in Fig. 11(a) note the vertical uniformity in the solid composition in comparison to the stratification observed in the initial design given in Reference [4].

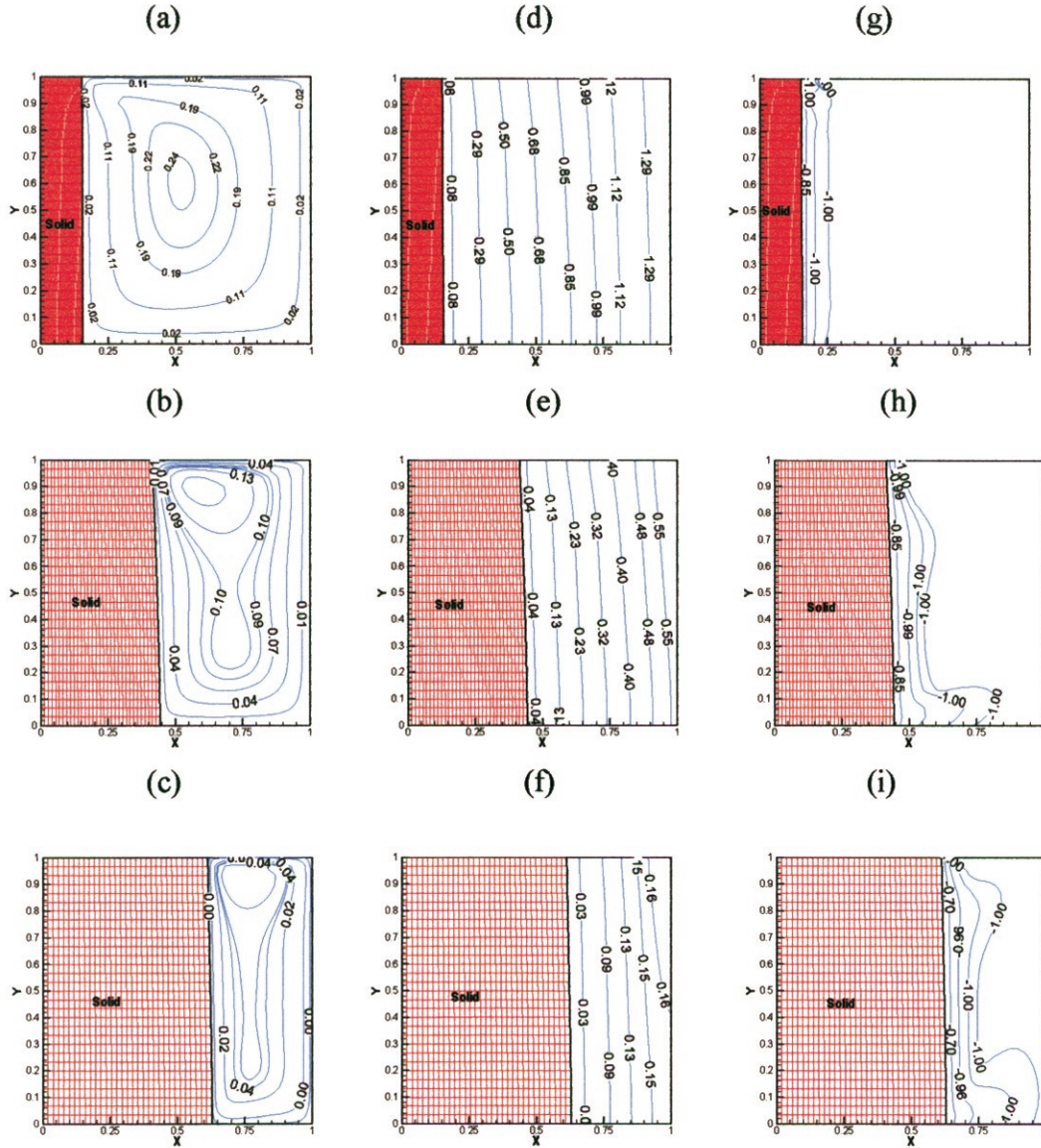


Figure 10: Contours of the fluid stream function (a-c), isotherms (d-f) and composition (g-i) for the optimal design eutectic solidification simulation. Results are shown at times $\tau = 0.1$, $\tau = 0.8$ and $\tau = 1.5$.

Further Developments

We are currently extending the above design algorithms to volume averaging based solidification models with main objectives the control of the solidification conditions within the mushy zone. A continuum sensitivity framework is being developed to allow us to perform gradient-based design optimization problems with the thermal boundary conditions, the level of gravity and the magnetic field being the main design variables. In contrast to the design problems discussed earlier, our design objectives are now defined within the mushy zone where all micro structural features are determined. In between various design problems, we are particularly interested at optimization problems that can be used to control the mushy zone morphology as well as the homogeneity of the solidified product.

Acknowledgements

This work is supported by the NASA microgravity materials science program (NRA-98-HEDS-05). Computing support was provided by the Cornell Theory Center.

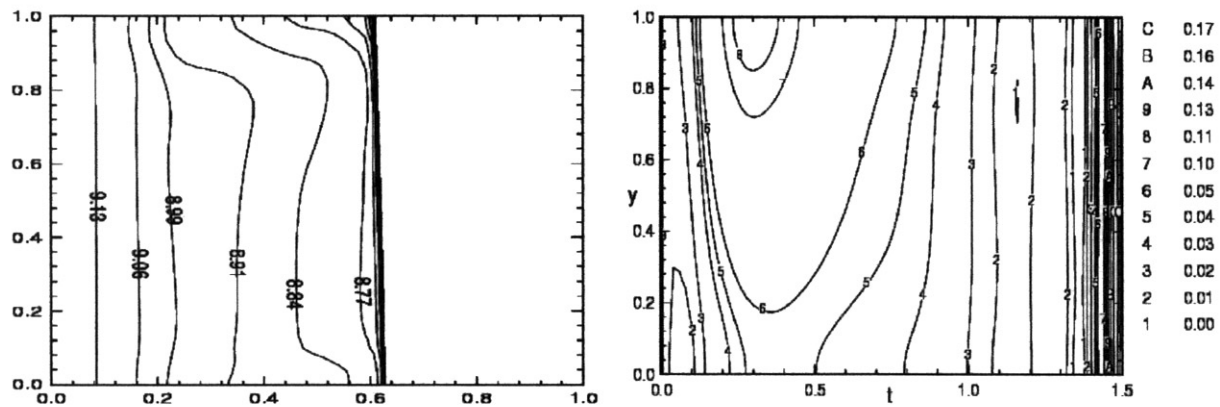


Figure 11: (a) The solid composition for the optimal solidification problem. The contours are labeled in wt% Germanium (b) dimensionless contours of $\Delta \equiv G/|\mathbf{v}_f| + m(C_E - C_o)/D_L$ are displayed. Notice that stable growth is achieved for the entire duration of solidification.

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ADVANCED ARC-DISCHARGE CARBON NANOTUBE GROWTH IN SIMULATED MICROGRAVITY: EFFECTS OF GEOMETRY AND ROTATIONS

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The objective of this study is to design, fabricate, and evaluate an arc-discharge set-up that simulates microgravity conditions and exploits the advantages of microgravity for the improved growth of single wall carbon nanotubes (SWCNT). These expected advantages are: (1) the growth of longer tubes with fewer defects and (2) an increased output and efficiency of SWCNT production. Another goal is to achieve selective separation of metallic nanotubes from semiconducting ones.

A major task was solved in the project: the construction of an arc-discharge chamber in which the geometry of the electrodes and the gas flows create conditions simulating microgravity. Contrary to conventional arc-discharge methods, which use two horizontal electrodes, our chamber utilized a large rotating electrode in center surrounded by electrodes from the top, bottom, and sides - thus simulating all possible directions of the gravitational field. The electrode was rotated to obtain a torroidal distribution of plasma. We discovered major differences in the product from these electrode symmetries. The convective flow of plasma and thermal conditions are quite different between horizontal and vertical electrode configurations. In the g-optimized case where the cathode was above the anode, there was a huge “mushroom” shaped deposit on the cathode rod containing 80 % SWCNT's. Deposits in the cathode contained graphitic carbon and multi-walled nanotubes. Long “webs” containing 40-50% SWCNT's formed on the upper walls of the chamber. Low density webs containing 30-40% SWCNT's were found on the bottom of the chamber. The upper part of the cathode rod was covered by a film-type felt contained 50 % SWCNTs. Synthesis of other materials such as N and B and the use of composite catalysts are also in progress.

Nanotubes synthesized by our methods have been used for the initial studies of the photo-acoustic effect upon illumination by light pulses from a Xenon flash lamp. Mass loss as a function of photon flux was measured. We accidentally found that the nanotubes are ignited by a flash of above approximately 3.50 mw/cm², and completely burn away in air. This phenomenon is now being studied in detail.

Keywords: single wall carbon nanotube, g-optimized arc, rotating electrode

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MEASUREMENT OF CHARGED PARTICLE INTERACTIONS IN SPACECRAFT AND PLANETARY HABITAT SHIELDING MATERIALS

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Abstract

Accurate models of health risks to astronauts on long-duration missions outside the geomagnetosphere will require a full understanding of the radiation environment inside a spacecraft or planetary habitat. This in turn requires detailed knowledge of the flux of incident particles and their propagation through matter, including the nuclear interactions of heavy ions that are a part of the Galactic Cosmic Radiation (GCR). The most important ions are likely to be iron, silicon, oxygen, and carbon. Transport of heavy ions through complex shielding materials – including self-shielding of tissue – modifies the radiation field at points of interest (e.g., at the blood-forming organs). The incident flux is changed by two types of interactions: (1) ionization energy loss, which results in reduced particle velocity and higher LET (Linear Energy Transfer); and (2) nuclear interactions that “fragment” the incident nuclei into less massive ions. Ionization energy loss is well understood, nuclear interactions less so. Thus studies of nuclear fragmentation at GCR-like energies are needed to fill the large gaps that currently exist in the database. These can be done at only a few accelerator facilities where appropriate beams are available. Here we report results from experiments performed at the Brookhaven National Laboratory’s Alternating Gradient Synchrotron (AGS) and the Heavy Ion Medical Accelerator in Chiba, Japan (HIMAC).

Recent efforts have focused on extracting charge-changing and fragment production cross sections from silicon beams at 400, 600, and 1200 MeV/nucleon. Some energy dependence is observed in the fragment production cross sections, and – as in other data sets – the production of fragments with even charge numbers is enhanced relative to those with odd charge numbers. These data are compared to the NASA-LaRC model NUCFRG2. The charge-changing cross section data are compared to recent calculations using an improved model due to Tripathi, which accurately predicts the observed (slight) energy dependence.

An additional set of data will be presented from an analysis of shielding material performance in the 1 GeV/nucleon iron beam at the AGS. A wide variety of candidate materials for spacecraft construction, as well as elemental targets, have been placed in this beam and their effects on transmitted dose and dose equivalent measured. The results support a prediction by J. Wilson et al. that hydrogen-loaded materials give the greatest dose reduction per unit mass.

Introduction

Three broad categories of space radiation are simulated in experiments performed by our group at ground-based particle accelerators: High-energy protons and ions (HZE) in the Galactic Cosmic Radiation (GCR); medium-energy protons from the GCR and from Solar Particle Events (SPE); and low-energy

Keywords: cosmic radiation, fragmentation, transport model

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trapped protons. In terms of absorbed dose, these are the most important particle types encountered by humans in space. GCR-like particle beams can be obtained at the AGS and HIMAC; medium-energy protons are available at the Loma Linda University Proton Treatment Center; and low-energy protons at energies approximating trapped protons are produced at the Lawrence Berkeley National Laboratory's 88" Cyclotron. In all of these categories, experimental data obtained by our group provide checks on model calculations, particularly those of the NASA-LaRC group, whose codes are used in spacecraft and spacesuit shielding models.

The experiments and calculations described here fall under two headings: fundamental physics relevant to the development of transport codes, and shielding materials studies. In the former category, we include measurements of cross sections for charged-particle production in HZE reactions [1, 2, 3] using elemental targets. The data obtained in these experiments are used for comparison to transport models, for example, the NASA-LaRC code NUCFRG2 [4] and others. The ultimate aim of the measurements is to fill in many of the holes in the existing database of cross sections for nucleus-nucleus interactions, which should lead to improvements in the semi-empirical portions of the transport codes. The second category of experiments, the shielding materials studies, includes iron-beam fragmentation measurements [5] using composite targets, performed primarily at the AGS.

Charged-particle Cross Sections in HZE Reactions

In these experiments, HZE ions at GCR-like energies are produced at the AGS and HIMAC, and elemental targets are placed in the path of the beam. The targets used are C, Al, Cu, Sn, Pb, and, in some recent experiments, a Li target has been used. Polyethylene (CH_2) is also; when cross sections obtained with the C target are subtracted from those with polyethylene, one obtains the cross sections on H, which are of particular interest for two reasons. First, and most relevant here, calculations [6] predict that hydrogenous materials provide superior shielding. Second, pertinent to astrophysics, the observed GCR flux is the result of transport from the sources through the interstellar medium, which is primarily hydrogen. Thus, accurate measurements of H-target cross sections are needed if the GCR composition at the source is to be understood.

The experiments described here use silicon detectors placed along beam axis (0°). Detectors are placed so as to subtend varying acceptance angles, as illustrated schematically in Fig. 1. Many data sets have been obtained at 0° , and a few data sets have been obtained with detectors placed off the beam axis, in order to make direct measurements of fragment angular distributions. The existing data on angular distributions are quite sparse.

Spectra obtained at 0° are used to extract the charge-changing and fragment production cross sections (σ_{cc} and σ_z), which depend on the species of the beam and target nuclei, and on the beam energy. Over the range of energies pertinent to the GCR, energy dependence of the cross sections is observed to be mild. As shown in Figure 2, significant differences are seen in spectra obtained with detectors placed at large acceptance (i.e., near the target exit, as in Fig. 2a) compared to spectra obtained with detectors further downstream (Fig. 2b). These differences give indirect information about fragment angular distributions. We note that virtually all previously published 0° measurements used only large acceptance detectors, and did not report cross sections for light fragments.

The spectrum in Fig. 2a illustrates the reason for the lack of light-fragment cross sections from earlier experiments: at large acceptance, there are simply no well-resolved fragment peaks below approximately

half the beam charge, making particle identification at the low end impossible. This is a consequence of the relatively high multiplicity of fragments produced when the incident beam ion undergoes a central collision and is broken up into many lighter nuclei. Because light fragments have relatively broad angular distributions, many of them are outside the acceptance of detectors placed far downstream of the target (i.e., at small acceptance). The reduction in observed multiplicity produces very clean spectra like the one in Fig. 2b. Note that although the fragment multiplicity is reduced at small acceptance angles, there are nonetheless several peaks in Fig. 2b that can only be explained by the presence of at least two fragments detected in coincidence, e.g., the peak near $Z = 3.5$, which is likely due to events in which three He fragments are detected. Other multiple-fragment peaks appear as shoulders just above the single-fragment peaks at 4, 5, 6, and 7. Another notable feature of Fig. 2b is the peak of approximately 3000 events (out of about 300,000 total) at $Z = 0$; these are events in which all the charged fragments were outside the acceptance of this detector.

Once the Z spectra are produced, a simple count of the numbers of events detected as a function of species is the main input to the calculation of the charge-changing and fragment production cross sections. Fig. 2 shows that even-charged fragments are preferentially produced, resulting in enhanced fragment production cross sections for those species, as illustrated in Fig. 3. The production of F ($Z = 9$) is particularly suppressed. Details such as these provide sensitive tests of models of nuclear interactions.

Charged-particle Fluences Behind Thick Targets

In a series of accelerator experiments similar to the cross-section measurements, we have placed thick, usually composite targets in the path of heavy ions beams. Most of our data have been acquired with the 1087 MeV/nucleon ^{56}Fe beam at the AGS. Fluence spectra have been obtained for many targets. Because the beam energy is relatively high, effects of fragmentation predominate over ionization energy-loss effects. Thus, in this beam, for any target material, the dose per particle exiting the target will be decreased relative to the dose per particle of the incident beam ions, provided the areal density is less than about 20 g cm⁻². (Especially at lower energies, there is a tradeoff between the two: Energy loss tends to increase LET and hence dose per particle, for those particles with sufficient energy to traverse the full depth of the target; fragmentation reactions, on the other hand, reduce the nuclear charge, reduces the dose per particle.) Despite this general trend, variations are still seen when we quantify the reduction in dose per particle reduction with different shielding materials.

The analysis of these data is simple. Starting with the LET of the 1087 MeV/nucleon AGS ^{56}Fe beam (148 keV/μm), using target-out data we determine a scale factor to convert the measured quantity (deposited energy, ΔE , in silicon) to LET. This factor is then applied to convert ΔE distributions acquired with targets in the beam to LET spectra. In a manner similar to that employed in the cross-section data analysis, we obtain counts of fragments and surviving primaries by species and apply (small) corrections for losses in the detector. The corrected counts are then used to obtain a corrected average LET, $\langle L \rangle$, which with this beam is invariably lower than the beam LET, L_{beam} . Because the targets are of modest depth and the beam energy is high, there are essentially no particles stopped in the target, and therefore (in the simplest approximation), the fluence exiting the target is equal to the incident fluence. Therefore $\langle L \rangle$ is directly proportional to the dose of the mixed field seen behind the target. For each target, we compute the fractional dose reduction per unit mass, given by $f = (1 - \langle L \rangle / L_{\text{beam}}) / (\rho * x)$ where $\rho * x$ is the areal density of the target. Results are shown below in Fig. 4.

In [6], Wilson *et al.* predict that hydrogenous materials will, in the space radiation environment, give the best performance per unit mass in terms of both dose equivalent and cell transformation probability. The results in Fig. 4, though not directly comparable, are qualitatively consistent with this prediction: the greatest dose reductions are seen with the Epoxy and Boron-Epoxy targets, which are hydrogen-rich. The Martian regolith simulant target also does well; it too has considerable hydrogen content (it consists of polyethylene blended with a mixture that approximates Martian soil). The smallest dose reductions are seen for elemental targets, Cu and Al (Pb data are also available but have not yet been analyzed for this purpose). Many more data sets have been obtained that can be applied to this analysis. Varying the beam ion and energy will provide a broader test of the relative performance of the different materials.

Summary

Extensive charged-particle measurements with GCR-like ions have been made for purposes of improving the nuclear cross section database and for direct measurements of shielding properties of various materials. Though considerable progress has been made in recent years, a large archive of data still awaits analysis and publication.

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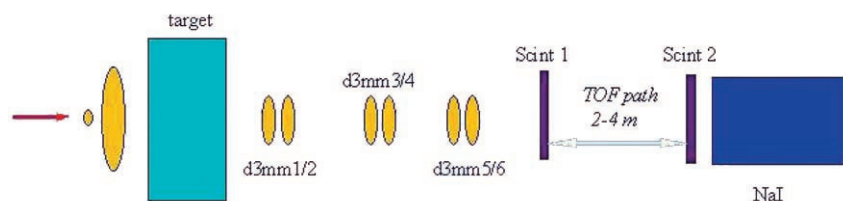


Figure 1. Schematic layout of charged-particle experiments at HIMAC. At the AGS, the TOF (time-of-flight) is not used due to the limited space available along the beamline.

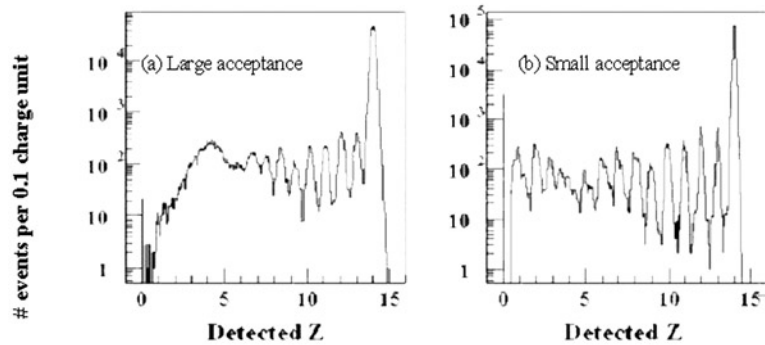


Figure 2. Spectra obtained with the 600 MeV/nucleon ^{28}Si beam at HIMAC incident on a 1.31 g cm^{-2} carbon target.

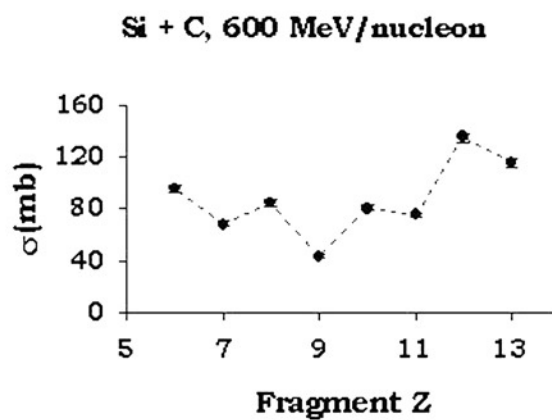


Figure 3. Fragment production cross sections for ^{28}Si on carbon at 600 MeV/nucleon, showing the “odd-even” effect (enhanced production of even- Z fragments).

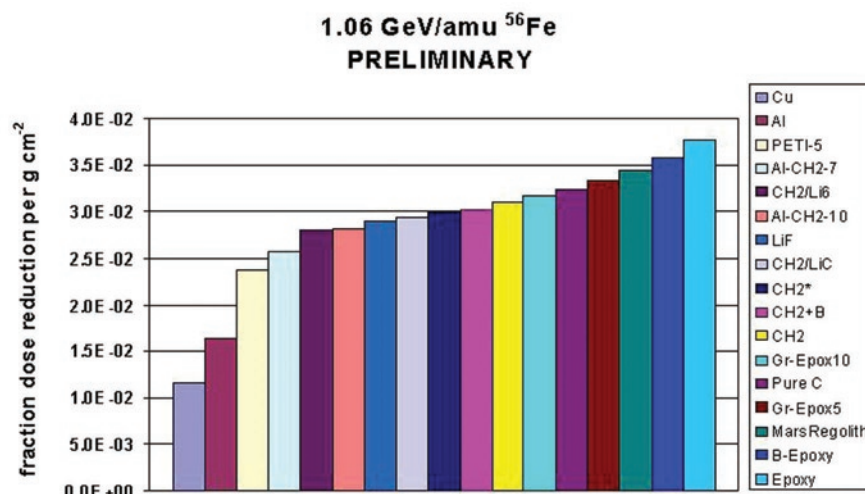


Figure 4. Dose reductions for various materials placed in the 1087 MeV/nucleon ^{56}Fe beam at the AGS. The list of target names in the legend, starting at the top, corresponds to the entries in the chart from left to right (i.e., the left-most chart entry is for the Cu target, followed by Al, PETI-5, etc.).

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Appendix B: Keyword Index

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Appendix C: Acronyms

Not included in this list are abbreviations for common chemical elements, units of measurement, or mathematical variables.

μ-g: microgravity	CCD: charge coupled device
1-g: one gravity	CELSS: Closed Environment Life Support Systems
2D: two dimensional	CFD: computational fluid dynamics software
3D: three dimensional	CGB: Crystal Growth using a Baffle
8YSZ: 8 mol% yttria stabilized zirconia	CGF: Crystal Growth Furnace
AA: acrylic acid	CGH: Coupled Growth in Hypermonotectics
AC: alternating current	CGM: conjugate gradient method
ACS: American Chemical Society	c-HA: carbonated crystalline hydroxyapatite
ADC: Analog to Digital Convertor	CMC: critical micellar concentration
ADP: ammonium dihydrogen phosphate	CMM: coordinate measuring machine
AFM: atomic force microscopy	CNL: conical nozzle levitation
AGHF: Advanced Gradient Heating Facility	CRI: Containerless Research, Inc.
AGS: Alternating Gradient Synchrotron	CRLR: Carbon-Based Reduction of Lunar Regolith
AHP: axial heat processing	CSLM: Coarsening in Solid Liquid Mixtures
NMR: nuclear magnetic resonance	CSRO: chemical short-range order
ALICE: A Large Ion Collisions Experiment	CT: computed tomography
AliROOT: ALICE Using ROOT	CVD: chemical vapor deposition
AOT: sodium bis(2-ethylhexyl) sulfosuccinate	DABCO: 1,4-diazabicyclo[2,2,2]octane
AP: ammonium persulfate	DARPA: Defense Advanced Research Projects Agency
MU-CAT: Advanced Photon Source at Argonne National laboratory	DBT: drop ball test
APS: advanced photon source	DC: detergent compatible
ASD: accelerated Stokesian dynamics	DC: direct current
ASTM: American Society of Testing and Materials	DFT: discrete Fourier transformation
ATD: advanced technology development	DLR: German Space Agency
ATIC: advanced thin ionization calorimeter	DLS: dynamic light scattering
AV: Akaiwa-Voorhees theory	DLVO: Derjaguin, Landau, Verwey and Overbeek Theory
BCT: Boettinger, Coriell, and Trivedi Theorem	DMA: differential mobility analyzer
BESL: beamline ESL	DMI: dimethylindium
BESSRC-CAT: beamline ID-11-C at the Advanced Photon Source	DMSO: dimethylsulfoxide
BG: bioactive glass	DMTA: Dynamic Mechanical Thermal Analyzer
BGO: bismuth-germanium-oxygen, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$	DOAP: Division of Amplitude Photopolarimeter
BMG: bulk metallic glasses	DODMAC: dimethyldioctylammonium chloride
BN/C: boron-nitrogen/carbon	DOE: Department of Energy
BNL AGS: Brookhaven National Laboratory Alternating Gradient Synchrotron	DPIMS: Diffusion Processes in Molten Semiconductors
CA: cellular automaton	DPM: Dual Parton Model
Cab-o-sil: fumed silica powder	DS: directional solidification
CAE: calcium aluminate eutectic	
CAM: CO_2 Acquisition Membrane	

DSC: differential scanning calorimetry
 DTA: differential thermal analysis
 EBS: ethylene-bis-stearamide
 EGDMA: ethylene glycol dimethacrylate
 EGS: Electron-Gamma Shower, transport codes
 for electron-photon transport
 EIT: effective interfacial tension
 EM: experiment module
 EML: electromagnetic levitation
 ESL: electrostatic levitation
 EVR: edge velocity ratio
 FAU: crystalline faujasite
 FCOM: fluorescence confocal optical microscopy
 FDLB: Finite Difference Lattice Boltzmann
 FEAST: Finite Element Analysis and Solution
 Tools
 FESEM: Field emission scanning electron
 microscopy
 FFT: fast Fourier transform
 FIDAP: Fluid Dynamics Analysis Package
 software
 FLEUR: FLUKA Executing Under ROOT
 FLUKA: A legacy acronym based on the German
 for FLUctuating KAscade
 FORTRAN: Formula Translation
 FTIR: Fourier transform infrared spectroscopy
 FZ: floating zone
 GaAs: gallium arsenide
 GaSb: gallium antimonide
 GCR: galactic cosmic radiation
 GDMS: glow discharge mass spectroscopy
 GEANT: GEometry and ANalysis Tool
 GFL: gas film levitation
 g-jitter: residual acceleration
 GLAD: Glass Liquids and Amorphous materials
 Diffractometer
 GUI: graphical user interface
 HARV: High Aspect Ratio Vessel
 HEDS: Human Exploration and Development of
 Space
 HETC: high energy transport code
 HIJING: Heavy Ion Jet INteraction Generator
 HIMAC: Heavy Ion Medical Accelerator in Chiba,
 Japan
 HPCVD: high-pressure chemical vapor deposition
 HS: hydrothermal
 HSDA: high speed data acquisition system
 HVESL: high vacuum electrostatic levitation
 HZE: high energy ions
 HZETRN: 1-D deterministic GCR transport code
 IBM: International Business Machines
 ICCA: Investment Casting Consortium
 Arrangement
 ICCG: International Conference on Crystal
 Growth
 ICP: inductively coupled plasma
 ICP-MS: inductively coupled plasma- mass
 spectrometry
 IDGE: Isothermal Dendritic Growth Experiment
 IFW-Dresden: Leibniz Institute for Solid State and
 Materials Research Dresden
 IMS: another name for Boettinger, Coriell, and
 Trivedi Theorem, see BCT.
 IPNS: intense pulsed neutron source
 IR: infrared
 ISRU: *in situ* resource utilization
 ISS: International Space Station
 ITO: indium-tin-oxide
 JANAF: thermodynamic data
 JSC: Johnson Space Center
 KDP: potassium dihydrogen phosphate
 kMC: kinetic Monte Carlo
 KOH: potassium hydroxide
 KSC: Kennedy Space Center
 LANSCE: Los Alamos Neutron Science Center
 LB: Langmuir-Blodgett
 LB: Lattice Boltzmann
 LC: liquid crystal
 LCDCs: liquid crystal dispersed colloids
 LED: light emitting diode
 LET: linear energy transfer
 LGK: Lipton, Glicksman and Kurz formulation
 LIF: laser induced fluorescence
 LKT: Lipton, Kurz and Trivedi theory
 LLPS: liquid-liquid phase separation
 LMS: Life and Microgravity Spacelab
 LOX: liquid oxygen
 LS2: lithium disilicate
 LSW: Lifshitz, Slyozov, and Wagner
 LVCC: laser vaporization controlled condensation

MAGG: multizone adaptive grid generation algorithm
 MASTRAPP: Multizone Adaptive Scheme for TRANsport and Phase-change Processes
 Matlab: a mathematical computer program
 MCA: membrane casting apparatus
 MD: molecular dynamics
 MEM: minimum essential medium
 MEPHISTO: Material pour l'Etude des Phenomenes Interessant la Solidification sur Terre et en Orbite
 MFI: polycrystalline films
 MG: Marsh and Glicksman theory
 MIM: Canadian microgravity isolation mount
 MIT: Massachusetts Institute of Technology
 MMI: monomethylindium
 MORSE: transport codes specialized for low-energy neutron transport
 MRD: NASA's Microgravity Research Division
 MSAD: NASA's Microgravity Sciences and Application Division
 MSE-UF/USA: Materials Science and Engineering-University of Florida/United States of America
 MSFC: Marshall Space Flight Center
 MSG: Microgravity Science Glovebox
 MSL-1R: Microgravity Science Laboratory Reflight
 MSRR: Materials Science Research Rack
 MST: microscopic solvable theory
 MST: minimum spanning tree
 MTF: membrane test facility
 MTV: molecular tagging velocimetry
 MV: macrovoid
 MWD: molecular weight distribution
 NASA: National Aeronautics and Space Administration
 NASA-LaRC: NASA's Langley Research Center
 NASDA: Japanese Space Agency
 NEB: nucleation energy barrier
 NEMS: nano-electro-mechanical systems
 NH₃: ammonia
 NIH: National Institutes of Health
 NIRS HIMAC: Heavy Ion Medical Accelerator at Chiba, National Institute of Radiological Sciences, Japan
 NMNH: National Museum of Natural History
 NS: Navier-Stokes
 NSB: Navier-Stokes-Boussinesq
 NSBRI: National Space Biomedical Research Institute
 NSF: National Science Foundation
 NUCFRG2: semi-empirical model for fragmentation
 OB: Oberbeck-Boussinesq
 OMCVD: organometallic chemical vapor deposition
 OO: object-oriented
 ORBITEC: Orbital Technologies Corporation
 P/S/NS: polymer/solvent/non-solvent
 PBG: photonic band gap
 PDFM: pseudopotential density functional method
 PDLCs : polymer dispersed liquid crystals
 PDMS: silicone rubber
 PEANUT: Pre-Equilibrium model
 PEC: polyelectrolyte complex
 PEG: polyethylene glycol
 PEP: Particle Engulfment and Pushing
 PFMI: Pore Formation and Mobility Investigation
 PI/ODMS: polyisoprene/oligomeric dimethylsiloxane
 PI: principal investigator
 PIB: polyisobutylene
 PIDs: photo ionization detectors
 PIV: particle image velocimetry
 PL: photoluminescence
 PMMA: polymethyl methacrylate
 PS/PDMS: polystyrene-polydimethylsiloxane
 PS/PMMA: polystyrene on polymethyl methacrylate
 PS-b-P2VP: polystyrene-block-poly2-vinylpyridine
 PSD: particle size distribution
 PVA FCC: pivalic acid, Face Centered Cubic Crystal
 PVA-EtOH: pivalic acid-ethanol
 PVT: physical vapor transport
 QMI: quench module insert
 RARAF: Columbia University Radiological Accelerator Research Facility

RDF: radial distribution function
 RGA: residual gas analysis
 RHIC: relativistic heavy ion collider
 RM: reverse micelle
 RMF: rotating magnetic field
 RPI: Rensselaer Polytechnic Institute
 RQMD: relativistic quantum molecular dynamics
 RWV: rotating wall vessel
 s/l: solid/liquid interface
 SAAL: Single Axis Acoustic Levitator
 SACA: sample ampoule cartridge assemblies
 SAMS: Space Acceleration Measurement System
 SAXS: small angle x-ray scattering
 SC: solutocapillary convection
 SCN: succinonitrile
 SCN-ACE: succinonitrile-acetone
 SCN-E: succinonitrile-ethanol
 SCN-W: succinonitrile-water
 SCR: science concept review
 SDA: structure-directing agent
 SDT: spinning drop tensiometer
 SEM: scanning electron microscopy
 SEP: solar energetic particles
 SGI: Silicon Graphics Inc.
 SHIVA: Spaceflight Holography Investigation in a Virtual Apparatus
 SHM: submerged heater method
 SHPB: split Hopkinson pressure bar
 SIAPM: semi-implicit approximate projection method
 SiLi: lithium drifted silicon
 SJT: solder jet technology
 SLI's: solid/liquid interfaces
 SMPC: Special Metal Processing Consortium
 SNR: signal-to-noise ratio
 SPE: solar particle events
 STS: Space Transportation System
 SUBSA: Solidification Using a Baffle in Sealed Ampoules
 SUNY: State University of New York
 SUPG/PSPG: streamline-upwind Petrov-Galerkin method/pressure-stabilizing Petrov-Galerkin method
 SWCNT: single wall carbon nanotubes
 TDSE: Time Dependant Schrödinger Equation
 TE: plasma
 TEM: tunneling electron microscopy
 TEMC: thermoelectromagnetic convection
 TES TE: plasma with 10% serum
 TGA: Thermal Gravimetric Analysis
 TGB: optical texture
 TGBC: twist grain boundary smectic C phase
 TIPMPS: Transient Interfacial Phenomena In Miscible Polymer Systems
 TLS: two-level system
 TMA⁺: tetramethylammonium ion
 TMF: traveling magnetic field
 TMI: trimethylindium
 TPA: tetrapropylammonium
 TPAOH: tetrapropylammonium hydroxide
 UA: University of Arizona
 UHP: ultra high purity
 ULSI: ultra large-scale integration
 USML: United States Microgravity Laboratory
 USMP: United States Microgravity Payload
 USRA: Universities Space Research Association
 UV: ultraviolet light
 VB: Vertical Bridgman
 VIRMCI: VIRTual Monte Carlo Interface
 VMFV: videomicroscopy flow-visualization
 VTR: video tape recorder
 WAXD: wide angle x-ray diffraction
 WAXS: wide angle x-ray scattering
 WKB: Wentzel, Kramers and Brillouin theory
 WSD: weighted spectral density
 WT: wild type protein
 XRD: X-ray diffraction
 YSZ: yttria-stabilized zirconia
 ZBLAN: Zirconium-Barium-Lanthanum-Aluminum-Sodium Fluoride glass

Appendix D: Contributor Websites

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Kenneth Jackson	http://www.optics.arizona.edu/Faculty/Resumes/Jackson.htm
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William Johnson	http://www.matsci.caltech.edu/
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